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(12) **United States Patent**
**Eastham et al.**

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(54) **PROCESS FOR THE CARBONYLATION OF ETHYLENICALLY UNSATURATED COMPOUNDS, NOVEL CARBONYLATION LIGANDS AND CATALYST SYSTEMS INCORPORATING SUCH LIGANDS**

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| ***B01J 31/04*** | (2006.01) |
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(52) **U.S. Cl.**

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(58) **Field of Classification Search**

None

See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

| | | | |
|---|---|---|---|
| 3,131,204 | A | 4/1964 | Sister et al. |
| 3,564,020 | A | 2/1971 | Fenton |
| 4,245,115 | A | 1/1981 | Butter |
| 4,377,708 | A | 3/1983 | Morris |
| 4,500,727 | A | 2/1985 | Kitamura et al. |
| 4,504,684 | A | 3/1985 | Fox et al. |
| 4,517,061 | A | 5/1985 | Fauvarque |
| 4,786,443 | A | 11/1988 | Drent et al. |
| 4,818,810 | A | 4/1989 | Drent |
| 4,835,250 | A | 5/1989 | Drent |
| 4,868,282 | A | 9/1989 | Van Broekhoven et al. |
| 4,880,903 | A | 11/1989 | Van Broekhoven et al. |
| 4,900,413 | A | 2/1990 | Tanaka et al. |
| 4,950,703 | A | 8/1990 | Smutny |

(Continued)

FOREIGN PATENT DOCUMENTS

| | | | |
|---|---|---|---|
| AU | 2003259322 | A1 | 2/2004 |
| AU | 2006314268 | A1 | 5/2007 |

(Continued)

OTHER PUBLICATIONS

Office Action issued in U.S. Appl. No. 12/084,575 dated Jan. 2, 2015.
Supplemental Notice of Allowance issued in U.S. Appl. No. 13/520,523 dated Feb. 10, 2015.

(Continued)

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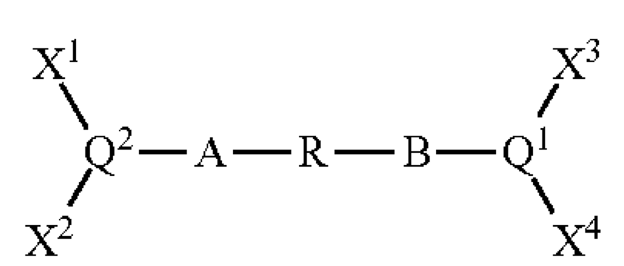
(57) **ABSTRACT**

A novel bidentate ligand of general formula (I)




(I)

is described together with a process for the carbonylation of ethylenically unsaturated compounds. The group $X^1$ may be defined as a univalent hydrocarbyl radical of up to 30 atoms containing at least one nitrogen atom having a pKb in dilute aqueous solution at 18° C. of between 4 and 14 wherein the said at least one nitrogen atom is separated from the $Q^2$ atom by between 1 and 3 carbon atoms. The group $X^2$ is defined as $X^1$, $X^3$ or $X^4$ or represents a univalent radical of up to 30 atoms having at least one primary, secondary or aromatic ring carbon atom wherein each said univalent radical is joined via said at least one primary, secondary or aromatic ring carbon atom(s) respectively to the respective atom $Q^2$. $Q^1$ and $Q^2$ each independently represent phosphorus, arsenic or antimony.

**27 Claims, No Drawings**

(56) **References Cited**

U.S. PATENT DOCUMENTS

| | | | |
|---|---|---|---|
| 4,960,926 | A | 10/1990 | Drent |
| 4,960,949 | A | 10/1990 | Devon et al. |
| 5,028,576 | A | 7/1991 | Drent et al. |
| 5,099,062 | A | 3/1992 | Drent et al. |
| 5,103,043 | A | 4/1992 | Drent et al. |
| 5,149,868 | A | 9/1992 | Drent |
| 5,158,921 | A | 10/1992 | Drent et al. |
| 5,166,116 | A | 11/1992 | Drent et al. |
| 5,177,253 | A | 1/1993 | Drent et al. |
| 5,179,225 | A | 1/1993 | Drent et al. |
| 5,189,003 | A | 2/1993 | Klusener et al. |
| 5,210,280 | A | 5/1993 | Drent |
| 5,245,098 | A | 9/1993 | Hamilton et al. |
| 5,246,558 | A | 9/1993 | Chevigne et al. |
| 5,258,546 | A | 11/1993 | Klusener et al. |
| 5,350,876 | A | 9/1994 | Drent et al. |
| 5,369,074 | A | 11/1994 | Drent |
| 5,436,356 | A | 7/1995 | Drent et al. |
| 5,563,308 | A | 10/1996 | Spindler et al. |
| 5,565,594 | A | 10/1996 | Spindler et al. |
| 5,618,983 | A | 4/1997 | Burke |
| 5,710,344 | A | 1/1998 | Breikss et al. |
| 5,719,313 | A | 2/1998 | Drent et al. |
| 5,760,264 | A | 6/1998 | Brieden |
| 5,773,661 | A | 6/1998 | Unruh et al. |
| 5,783,715 | A | 7/1998 | Pugin |
| 5,962,732 | A | 10/1999 | Burke |
| 6,015,919 | A | 1/2000 | Pugin |
| 6,156,934 | A | 12/2000 | Suykerbuyk et al. |
| 6,169,192 | B1 | 1/2001 | Pugin et al. |
| 6,191,284 | B1 | 2/2001 | Knochel et al. |
| 6,232,262 | B1 | 5/2001 | Sielcken et al. |
| 6,258,979 | B1 | 7/2001 | Kagan et al. |
| 6,284,919 | B1 | 9/2001 | Pearson et al. |
| 6,284,925 | B1 | 9/2001 | Knochel et al. |
| 6,307,065 | B1 | 10/2001 | Tjaden et al. |
| 6,335,471 | B1 | 1/2002 | Eastham et al. |
| 6,337,406 | B1 | 1/2002 | Zhang |
| 6,348,621 | B1 | 2/2002 | Wang et al. |
| 6,391,818 | B1 | 5/2002 | Bonsel et al. |
| 6,462,095 | B1 | 10/2002 | Bonsel et al. |
| 6,476,255 | B1 | 11/2002 | Hadden et al. |
| 6,521,769 | B1 | 2/2003 | Zhang |
| 6,706,912 | B2 | 3/2004 | Drent et al. |
| 6,723,882 | B2 | 4/2004 | Slany et al. |
| 6,737,542 | B1 | 5/2004 | Drent et al. |
| 6,743,911 | B2 | 6/2004 | Drent et al. |
| 6,753,450 | B2 | 6/2004 | Ahlers et al. |
| 6,844,463 | B2 | 1/2005 | Slany et al. |
| 6,916,954 | B2 | 7/2005 | Schafer et al. |
| 6,982,357 | B2 | 1/2006 | Crabtree et al. |
| 6,984,668 | B1 | 1/2006 | Eastham et al. |
| 7,026,473 | B2 | 4/2006 | Drent et al. |
| 7,129,367 | B2 | 10/2006 | Suzuki et al. |
| 7,148,176 | B2 | 12/2006 | Beller et al. |
| 7,265,240 | B2 | 9/2007 | Eastham et al. |
| 7,371,705 | B2 | 5/2008 | Eastham et al. |
| 7,629,470 | B2 | 12/2009 | Campos et al. |
| 8,604,236 | B2 | 12/2013 | Eastham et al. |
| 9,040,445 | B2 | 5/2015 | Eastham et al. |
| 2001/0044556 | A1 | 11/2001 | Drent et al. |
| 2001/0051745 | A1 | 12/2001 | Pearson et al. |
| 2002/0016484 | A1 | 2/2002 | Drent et al. |
| 2002/0045748 | A1 | 4/2002 | Drent et al. |
| 2003/0191339 | A1 | 10/2003 | Schfer et al. |
| 2004/0110989 | A1 | 6/2004 | Slany et al. |
| 2004/0115475 | A1 | 6/2004 | Hashimoto |
| 2004/0162440 | A1 | 8/2004 | Bunel et al. |
| 2005/0090694 | A1 | 4/2005 | Drent et al. |
| 2006/0106259 | A1 | 5/2006 | Eastham et al. |
| 2006/0122435 | A1 | 6/2006 | Eastham et al. |
| 2006/0128985 | A1 | 6/2006 | Eastham et al. |
| 2006/0235241 | A1 | 10/2006 | Drent et al. |
| 2006/0252935 | A1 | 11/2006 | Eastham et al. |
| 2008/0051475 | A1 | 2/2008 | Eastham et al. |
| 2008/0086015 | A1 | 4/2008 | Eastham |
| 2008/0269459 | A1 | 10/2008 | Drent et al. |
| 2008/0269520 | A1 | 10/2008 | Drent et al. |
| 2009/0163724 | A1 | 6/2009 | Eastham et al. |
| 2009/0216041 | A1 | 8/2009 | Eastham et al. |
| 2009/0234126 | A1 | 9/2009 | Hartwig et al. |
| 2009/0312561 | A1 | 12/2009 | Eastham et al. |
| 2010/0030036 | A1 | 2/2010 | Mottram et al. |
| 2010/0113255 | A1 | 5/2010 | Eastham et al. |
| 2010/0197958 | A1 | 8/2010 | Eastham et al. |
| 2010/0324332 | A1 | 12/2010 | Carrington-Smith et al. |
| 2012/0010413 | A1 | 1/2012 | Abrecht et al. |

FOREIGN PATENT DOCUMENTS

| | | | |
|---|---|---|---|
| BR | PI 9000965 | A | 2/1991 |
| BR | PI 9510249-3 | A | 11/1997 |
| BR | PI 0109239 | A | 12/2002 |
| BR | PI 0313289-7 | A | 7/2005 |
| CA | 2498293 | A1 | 3/2004 |
| CN | 1171098 | A | 1/1998 |
| CN | 1429228 | A | 7/2003 |
| CN | 1478071 | A | 2/2004 |
| CN | 101137611 | A | 3/2008 |
| CN | 101142162 | A | 3/2008 |
| DE | 19745904 | A1 | 4/1999 |
| DE | 19754304 | A1 | 6/1999 |
| DE | 10023470 | A1 | 11/2001 |
| DE | 10037961 | A1 | 2/2002 |
| EP | 0055875 | A1 | 7/1982 |
| EP | 0106379 | A1 | 4/1984 |
| EP | 121965 | A2 | 10/1984 |
| EP | 0144118 | A1 | 6/1985 |
| EP | 181014 | A1 | 5/1986 |
| EP | 213671 | A1 | 3/1987 |
| EP | 0 227 160 | A2 | 7/1987 |
| EP | 0235864 | A1 | 9/1987 |
| EP | 0274795 | A2 | 7/1988 |
| EP | 0282142 | A1 | 9/1988 |
| EP | 0305089 | A1 | 3/1989 |
| EP | 0375573 | A1 | 6/1990 |
| EP | 0386833 | A1 | 9/1990 |
| EP | 0441447 | A1 | 8/1991 |
| EP | 0489472 | A2 | 6/1992 |
| EP | 0 495 548 | A2 | 7/1992 |
| EP | 0495347 | A1 | 7/1992 |
| EP | 0495348 | A1 | 7/1992 |
| EP | 0495547 | A2 | 7/1992 |
| EP | 0 499 329 | A1 | 8/1992 |
| EP | 0577205 | A2 | 1/1994 |
| EP | 0683764 | A1 | 11/1995 |
| EP | 0728733 | A1 | 8/1996 |
| EP | 0879642 | A2 | 11/1998 |
| EP | 1330309 | A1 | 7/2003 |
| FR | 2034147 | A5 | 12/1970 |
| GB | 2006208 | A | 5/1979 |
| JP | 6216737 | A | 1/1987 |
| JP | 04-215851 | A | 8/1992 |
| JP | H0558949 | A | 3/1993 |
| JP | 06-065148 | A | 3/1994 |
| JP | 08134218 | A | 5/1996 |
| JP | 10-511034 | A | 10/1998 |
| JP | 10 339929 | A | 12/1998 |
| JP | 2001-517218 | A | 10/2001 |
| JP | 2003-527365 | A | 9/2003 |
| JP | 2003-528849 | A | 9/2003 |
| JP | 2004-509741 | A | 4/2004 |
| JP | 2004-515487 | A | 5/2004 |
| JP | 2004-515537 | A | 5/2004 |
| JP | 2005-535455 | A | 11/2005 |
| JP | 2005-535695 | A | 11/2005 |
| JP | 2007-502315 | A | 2/2007 |
| JP | 2007-524700 | A | 8/2007 |
| JP | 2008-505903 | A | 2/2008 |
| JP | 2009-504620 | A | 2/2009 |
| JP | 2009-515936 | A | 4/2009 |
| JP | 2009-533409 | A | 9/2009 |
| JP | 2010511600 | A | 4/2010 |
| JP | 2013063440 | A | 4/2013 |

(56) **References Cited**

FOREIGN PATENT DOCUMENTS

| | | | |
|---|---|---|---|
| JP | 2013-091651 | A | 5/2013 |
| JP | 5198267 | B2 | 5/2013 |
| JP | 2013-147503 | A | 8/2013 |
| JP | 5350592 | B2 | 11/2013 |
| JP | 2014-208649 | A | 11/2014 |
| KR | 2000-0076427 | | 12/2000 |
| KR | 20050084042 | A | 8/2005 |
| KR | 10-0851423 | B1 | 8/2008 |
| TW | 524801 | B | 3/2003 |
| TW | 552257 | B | 9/2003 |
| TW | 200416212 | | 9/2004 |
| TW | 200404773 | | 4/2010 |
| TW | I410280 | B | 10/2013 |
| WO | WO-96/19434 | A1 | 6/1996 |
| WO | WO-97/08124 | A1 | 3/1997 |
| WO | WO-97/40001 | A1 | 10/1997 |
| WO | WO-98/41495 | A1 | 9/1998 |
| WO | WO-98/42717 | A1 | 10/1998 |
| WO | WO-98/45040 | A1 | 10/1998 |
| WO | WO-99/47528 | A1 | 9/1999 |
| WO | WO-00/56695 | A1 | 9/2000 |
| WO | WO-01/10551 | A1 | 2/2001 |
| WO | WO-01/28972 | A1 | 4/2001 |
| WO | WO-01/38336 | A1 | 5/2001 |
| WO | WO-01/65583 | A1 | 9/2001 |
| WO | WO-01/70659 | A1 | 9/2001 |
| WO | WO-0168583 | A2 | 9/2001 |
| WO | WO-01/72697 | A2 | 10/2001 |
| WO | WO-01/85662 | A2 | 11/2001 |
| WO | WO-0187899 | A1 | 11/2001 |
| WO | WO-02/12161 | A1 | 2/2002 |
| WO | WO-02/46143 | A1 | 6/2002 |
| WO | WO-02/48094 | A1 | 6/2002 |
| WO | WO-03/040159 | A2 | 5/2003 |
| WO | WO-03/070370 | A1 | 8/2003 |
| WO | WO-2004/014552 | A1 | 2/2004 |
| WO | WO-2004/014834 | A1 | 2/2004 |
| WO | WO-2004/024322 | A2 | 3/2004 |
| WO | WO-2004/028689 | A2 | 4/2004 |
| WO | WO-2004/050599 | A1 | 6/2004 |
| WO | WO-2004050599 | A1 | 6/2004 |
| WO | WO-2004/072088 | A2 | 8/2004 |
| WO | WO-2004/103948 | A1 | 12/2004 |
| WO | WO-2005/003070 | A1 | 1/2005 |
| WO | WO-2005/079981 | A1 | 9/2005 |
| WO | WO-2005/082830 | A1 | 9/2005 |
| WO | WO-2005/118519 | A1 | 12/2005 |
| WO | WO-2006/062467 | A1 | 6/2006 |
| WO | WO-2006/084892 | A2 | 8/2006 |
| WO | WO-2007/020379 | A1 | 2/2007 |
| WO | WO-2007109365 | A2 | 9/2007 |
| WO | WO-2007/119079 | A1 | 10/2007 |
| WO | WO-2007119079 | A1 | 10/2007 |
| WO | WO-2008/031750 | A2 | 3/2008 |
| WO | WO-2008/065448 | A1 | 6/2008 |
| WO | WO-2008/075108 | A1 | 6/2008 |
| WO | WO-2008145976 | A1 | 12/2008 |
| WO | WO-2009010782 | A1 | 1/2009 |

OTHER PUBLICATIONS

Office Action issued in U.S. Appl. No. 13/516,176 dated Mar. 6, 2015.

Office Action issued in U.S. Appl. No. 12/084,575 dated Jul. 24, 2015.

Office Action issued in U.S. Appl. No. 12/517,215 dated Jul. 21, 2015.

Office Action issued in U.S. Appl. No. 13/516,176 dated Aug. 19, 2015.

"Basic Energy Sciences Advisory Committee Subpanel Workshop Report," Opportunities for catalysis in the 21st century, 2002, p. 1-46.

Hessler et al., "Synthesis and coordination chemistry of hemilabile P, N-hybrid ligands with terminal 2-pyridyl or groups," Chemische Berichte, Germany 1994, 127(3): 481-488.

Hessler et al., "Water Soluble Cationic Phosphine Ligands Containing m-Guanidinium Phenyl Moieties," Syntheses and Applications in Aqueous Heck Type Reaactions, Journal of Organic Chemistry, 1997, 62(8): 2362-2369.

Office Action issued in U.S. Appl. No. 13/516,176 dated Jan. 22, 2016.

Office Action issued in U.S. Appl. No. 12/517,215 dated Jan. 4, 2016.

Notice of Allowance issued in U.S. Appl. No. 12/084,575 dated Jan. 14, 2016.

Notice of Allowance issued in U.S. Appl. No. 13/520,523 dated Oct. 14, 2014.

Office Action issued in U.S. Appl. No. 12/517,215 dated Nov. 14, 2014.

Office Action issued in U.S. Appl. No. 13/516,176 dated Oct. 9, 2014.

Notice of Allowance issued in U.S. Appl. No. 10/589,971 dated Dec. 5, 2014.

Kraatz et al., "The reactions of tridentate cationic palladium (II) complexes with olefins and nucleophiles," The Journal of Organometallic Chemistry, vol. 488, No. 1, pp. 223-232 (1995).

United Kingdom Search Report issued in Application No. GB 1000078.4 dated May 6, 2010.

Vavasori et al., "Carbon monoxide-ethylene copolymerization catalyzed by a $Pd(AcO)_2$/dpppTsOH[1] system: the promoting effect of water and of the acid", Journal of Molecular Cat. A. Chem., vol. 110, 1996, Abstract.

Vavasori et al., "Highly active $[Pd(AcO)_2(dppp(]$ catalyst for the $CO—C_2H_4$ copolymerization in $H_2O—CH_3COOH$ solvent [dppp = 1,3-bis (diphenylphosphino)propane]" Journal of Molecular Cat. A. Chem., vol. 204-205, 2003, pp. 295-303.

Seayad et al., "Hydroesterification of styrene using an in situ formed $Pd(OTs)_2(PPh_3)_2$ complex catalyst", Journal of Molecular Cat. A. Chem., vol. 151, 2000, pp. 47-59.

Abbenhuis et al., "Successful Application of a "Forgotten" Phosphine in Asymmetric Catalysis: A 9-Phosphabicyclo[3.3.1]non-9-yl Ferrocene Derivative as a Chiral Ligand," Organometallics, vol. 14, pp. 759-766, 1995.

Andrews et al. "Regioselective complexation of unprotected carbohydrates by Platinum(II); Synthesis, structure, complexation equilibria, and hydrogen-bonding in carbonate-derived bis(phosphine)platinum(II) diolate and alditolate complexes", Journal of American Chemical Society, No. 116, pp. 5730-5740, (1994).

Andrews et al. "Syntheses, spectra and structures of (diphosphine)platinum(II) carbonate complexes" Inorganic Chemistry, No. 35, pp. 5478-5483, (1996).

Armor, "Perspective: Do you really have a better catalyst?," Applied Catalysis A: General, vol. 282, pp. 1-4, 2005.

Becker et al. "Imprinting chiral information into rigidified dendrimers", Organometallics, No. 22, pp. 4984-4998, (2003).

Becker et al, "Synthesis and characterization of chiral diphosphine platinum(II) VANOL and VAPOL complexes", Organometallics, No. 22, pp. 3245-3249, (2003).

Bellabarba et al., "Synthesis, X-ray characterization and reactions of a trigonal planar palladium()) carbonyl complex", Chemical Communications, No. 15, pp. 1916-1917, (2003).

Brauer et al., "Reactions of coordinated ligands. XIV. Synthesis of a tetradentate phosphorus macrocycle in a palladium (II) template", Chemische Berichte, vol. 119, No. 1, pp. 349-365 (1986).

Brunkan et al. "Effect of chiral cavities associated with molecularly imprinted platinum centers on the selectivity of ligand-exchange reactions at platinum", Journal of American Chemical Society, No. 22, pp. 6217-6225, (2000).

Brunkan et al. "Unorthodox C,O binding mode of $Me_2$BINOL in Pt(II) complexes", Journal of American Chemical Society, No. 120, pp. 11002-11003, (1998).

Cecconi et al. "Palladium complexes with the tripodal phosphine tris(2-diphenylphosphinoethyl)amine. Synthesis and structure of trigonal, tetrahedral, trigonal bipyramidal, and square planar complexes", J. Chem. Soc. Dalton Trans., issue 1, pp. xvii-xx. (1989).

Clegg et al., "Characterisation and dynamics of [Pd(L-L)H(solv)]+, [Pd(L-L(CH2CH3)]+ and [Pd(L-L)(C(0)Et)(THF)]+ (L-L=1,2-(CH2PBut2)2C6H4): key intermediates in the catalytic methoxycarbonylation of ethane to methylpropanoate", Organometallics, vol. 21, No. 9, pp. 1832-1840 (2002).

(56) **References Cited**

OTHER PUBLICATIONS

Clegg et al., "Synthesis and reactivity of palladium hydrido-solvento complexes, including a key intermediate in the catalytic methoxycarbonylation of ethane to methypropanoate", Journal of the Chemical Society, Dalton Transactions, No. 17, pp. 3300-3308 (2002).
Cullen et al, "Structure of the Hydrogenation Catalyst $[(PP)Rh(NBD)]ClO_4$, $(PP)=(\eta 5\text{-}[(CH_3)_3C]_2PC_5H_4)_2Fe$, and Some Comparative Rate Studies," Organometallics, vol. 2, pp. 714-719, 1983.
Dias et al., "Synthesis and characterization of .eta.5-monocyclopentadienyl (p-nitrobenzonitrile)ruthenium(II) salts: second harmonic generation powder efficiencies", Journal of Organometallic Chemistry, vol. 475, No. 1-2, pp. 241-245 (1994).
Edelbach et al., "Catalytic hydrogenolysis of biphenylene with platinum, palladium, and nickelphosphine complexes", Organometallics, vol. 17, No. 22, pp. 4784-4794 (1998).
Grimmer, et al., "Zirconium *bis*-cyclopentadienyl compounds: An investigation into the influence of substituent effects on the ethene polymerisation behaviour of $(CpR)_2ZrCl_2$/MAO catalysts," Journal of Molecular Catalysis A: Chemical, vol. 188, No. 1-2, pp. 105-113, 2002.
Hagen, "Industrial Catalysis: A Practical Approach," pp. v-xvii and 1-6, 2006.
Hartley, Supported Metal Complexes: A New Generation of Catalysts, Section 1.3, pp. 1, 9, 1985.
Hartwig, et al. "Structure and reactions of oxametallacyclobutanes and oxametallacyclobutenes of ruthenium", Organometallics, vol. 10, No. 9, pp. 3344-3362 (1991).
Hayward et al. "Some reactions of peroxobis (triphenylphosphine)platinum(II) and analogs with carbon dioxide, carbon disulfide, and other unsaturated molecules", Journal of American Chemical Society, vol. 92, issue 20, pp. 5873-5878, (1970).
Hofmann et al., "Bis(Di-T-Butylphosphino)Methane Complexes of Rhodium: Homogeneous Alkyne Hydrosilylation by Catalyst-Dependent Alkyne Insertion Into Rh—Si or Rh—H Bonds, Molecular Structures of the Dimer $[(dtbpm)\ RHcL]_2$ and of the Silyl Complex (dtbpm) Rh[Si(OEt)$^{3](PMe}$3)", Journal of Organometallic Chemistry, vol. 490, 1995, pp. 51-70.
International Search Report issue in GB0624114.5 dated Mar. 30, 2007.
International Search Report issue in GB0716530.1 dated Jan. 30, 2008.
Jones et al, "Rhodium-Catalyzed Activation and Functionalization of the C—C Bond of Biphenylene", Organometallics, vol. 20, 2001, pp. 5745-5750.
Kim et al., "Synthesis and theoretical study of palladium (II) complexes with aminophosphines as 7-membered chelate rings", Bulletin of the Korean Chemical Society, vol. 18, No. 11, pp. 1162-1166 (1997).
Kirk Othmer Encyclopaedia of Chemical Terminology, vol. 9, 4th Ed., p. 783, Hydrolysis of Organic Esters, pp. 783-85 and 87, John Wiley & Sons, Jan. 1994.
Knight et al: "Remarkable Differences in Catalyst Activity and Selectivity fo rthe production of Methyl Propanoate versus CO-Ethylene Copolymer by a Series of palladium Complexes of Related $C_4$-Bridged Diphosphines" Organometallics 2000, 19 4957-4967.
Konno et al. "Preparation and spectroscopic characteristics of geometrical isomers of bis[1,2-bis(dimethylphosphino)ethane]cobalt(III) complexes with thiolate ligands", The Chemical Society of Japan, No. 62, pp. 3475-3478, (1989).
Latif et al. "Square planar platinum(II) complexes, crystal structures of *cis*-bis(triphenylphosphine) hydro(triphenyistannyl) platinum(II) and *cis*-bis(triphenylphosphine) hydro(triphenylsilyl) platinum(II)", Journal of Organometallic Chemistry, No. 474, pp. 217-221, (1994).
Lide et al., Handbook of Chem and Phys., 76th Ed., CRC Press, 1995, ps. 8-141 6-155 to 6-177; 15-16 to 15-25.
Lindner et al., "Catalytic Activity of Cationic Diphospalladium (II) Complexes in the Alkene/Co Copolymerization in Organic Solvents and Water in Dependence on the Length of the Alkyl Chain At the Phosphine Ligands", Journal of Organometallic Chemistry, vol. 602, 2000, pp. 173-187.
Machine Translation of JP 08-134218, May 28, 1996.
Masters et al. "Homogeneous Transition Metal Catalysis—A Gentle Art", C Masters, Chapman & Hall, Feb. 1981, title page, contents page and pp. 4-21.
Masters, Christopher, "Homogeneous transition-mental catalysis", London, New York, Shapaman and Hall, pp. 1-21.
Mikami et al. "Molecular design of DABNTf as a highly efficient resolving reagent for racemic Pd complex with *tropos* biphenylphosphine (BIPHEP) ligand: circular dichroism (CD) spectra of enantiopure BIPHEP-Pd complex", Chirality, No. 15, pp. 105-107, (2003).
Miskowski et al. "Preparation and spectroscopic properties of Cobalt(III) complexes containing phosphine ligands. The electronic structural description of side-bonded dioxygen", Journal of American Chemical Society, vol. 98, No. 9, pp. 2477-2483, (1976).
Molander et al., "Synthesis and application of chiral cyclopropane-based ligands in palladium-catalyzed allylic alkylation", Journal of Organic Chemistry, vol. 69, No. 23, pp. 8062-8069 (2004).
Oblad et al., Catalysis and Catalysts. In McKetta ed, *Encyclopedia of Chemical Processing and Design*, pp. 420-490, 1978.
Office Action for U.S. Appl. No. 10/536,801, issued by the USPTO on Apr. 8, 2008.
Office Action for U.S. Appl. No. 10/536,801, issued by the USPTO on Jan. 7, 2010.
Office Action for U.S. Appl. No. 10/536,801, issued by the USPTO on Jun. 17, 2009.
Office Action for U.S. Appl. No. 10/561,912, issued by the USPTO on Aug. 25, 2008.
Office Action for U.S. Appl. No. 10/561,912, issued by the USPTO on Feb. 11, 2009.
Office Action for U.S. Appl. No. 10/561,912, issued by the USPTO on Jan. 14, 2008.
Office Action for U.S. Appl. No. 10/561,912, issued by the USPTO on Sep. 2, 2009.
Office Action for U.S. Appl. No. 10/589,971, issued by the USPTO on Jul. 27, 2010.
Office Action for U.S. Appl. No. 10/589,971, issued by the USPTO on Mar. 22, 2011.
Office Action for U.S. Appl. No. 11/597,787, issued by the USPTO on May 20, 2009.
Office Action for U.S. Appl. No. 11/597,787, issued by the USPTO on Oct. 8, 2008.
Office Action for U.S. Appl. No. 11/597,787, issued by the USPTO on Oct. 8, 2009.
Office Action for U.S. Appl. No. 11/990,272, issued by the USPTO on Jul. 12, 2011.
Office Action issued by the USPTO in U.S. Appl. No. 12/518,320 on Dec. 8, 2010.
Olah, George A., et al., "$AlCl_3$-Catalyzed Dichlorophosphorylation of Saturated Hydrocarbons with $PCl_3$ in Methylene Chloride Solution," *J. Org. Chem.*, 1990, 55, 1224-1227.
Osman, Serindag "Synthesis of some platinum(II) diphosphine complexes of the type $[PtX_2(P\text{-}P)]$ ($X_2$=$CO_3$; X=$CH_3COO$, $CF_3COO$, NCO)", Synth. React. Inorg. Met.-Org. Chem., vol. 27. No. 1, pp. 69-76, (1997).
Peng et al. "Chiral rodlike platinum complexes, double helical chains and potential asymmetric hydrogenation ligand based on "linear" building blocks: 1,8,9,16-tetrahydroxytetraphenylene and 1,8,9,16-tetrakis(diphenylphosphino)tetraphenylene" Journal of American Chemical Society, No. 127, pp. 9603-9611, (2005).
Portnoy et al., "Reactions of electron-rich arylpalladium complexes with olefins. Origin of the chelate effect in vinylation catalysis", Organometallics, vol. 13, No. 9, pp. 3465-3479 (1994).
Pugh, R. I. et al. "Tandem isomerisation-carbonylation catalysis: highly active palladium(II) catalysts for the selective methoxycarbonylation of internal alkenes to linear esters", Chemical Communications—CHEMCOM, Royal Society of Chemistry, GB, No. 16, (Aug. 21, 2001), pp. 1476-1477.

(56) **References Cited**

OTHER PUBLICATIONS

Reddy et al., "Unexpected cross-metathesis between Si-C and Si-Si bonds", Chemical Communications, No. 16, pp. 1865-1866 (1996).
Related U.S. Appl. No. 10/524,023, filed Nov. 17, 2005, Eastham et al.
Richmond et al., "Preparation of New Catalysts by the Immobilization of Palladium(II) Species Onto Silica: An Investigation of Their Catalytic Activity for the Cyclization of Aminoalkynes", J. Am Chem. Soc., vol. 123, 2001, pp. 10521-10525.
Tamao et al., "Alkyl Group Isomerization in the Cross-Coupling Reaction of Secondary Alkyl Grignard Reagents With Organic Halides in the Presence of Nickel-Phosphine Complexes As Catalysts", Journal of the American Chemical Society, vol. 94, 1972, pp. 9268-9269.
Tanaka et al., "Synthesis of ketones via carbonylation of organic halides. II. Palladium-catalysed carbonylation of organic halides with terminal acetylenes in the presence of amines. Novel acetylenic ketone synthesis", Nippon Kagaku Kaishi, No. 3, pp. 537-546 (1985).
Tolman, "Phosphorous Ligand Exchange Equilibria on Zerovalent Nickel. A Dominant Role for Steric Effects," Journal of the American Chemical Society, vol. 92, No. 10, pp. 2956-2965, 1970.
Tolman, "Steric Effects of Phosphorous Ligands in Organometallic Chemistry and Homogeneous Catalysis," Chemical Reviews, vol. 77, No. 3, pp. 313-348, 1977.
Tudor et al. "Diasteroisomer interconversion in chiral BiphepPt$X_2$ complexes", Organometallics, No. 19, pp. 4376-4384, (2000).
Uchimaru et al., "Ring-opening polymerization of 1,1,2,2-tetramethyl-1,2-disilacyclopentane via palladium complex-catalysed Si-Si bond metathesis", Chemistry Letters, No. 2, p. 164 (1995).
Wang et al., "Polymer-Bound Bidentate-Phosphine-Pallalium Complex as a Catalyst in the Heck Arylation", J. Org. Chem, vol. 59, No. 18, 1994, pp. 5358-5364.
Wei-Yong Yu, et al., "Preparation of Polymer-Protected Pt/Co Bimetallic Colloid and its Catalytic Properties in Selective Hydrogenation of Cinnamaldehyde to Cinnamyl Alcohol," Polymers for Advanced Technologies, GB, John Wiley and Sons, Chichester, Aug. 1, 1996, 719-722, vol. 7, No. 8.
Wen et al. "Synthesis, resolution, and applications of 1,16-dihydroxytetraphenylene as a novel building block in molecular recognition and assembly", Journal of Organic Chemistry, No. 68, pp. 8918-8931, (2003).
Written Opinion of the International Searching Authority, issued in PCt/GB2007/050189 filed Apr. 10, 2007.
Wurst et al., "Synthesis and structure of the platinum (0) compounds [(dipb)Pt]2(COD) and (dipb)3Pt2 and of the cluster Hg6[Pt(dipb)]4 (dipb=(iPr)2P(CH2)4P(i-Pr)2)", Zeitschrift Für Anorganische Und Allgemeine Chemie, vol. 395, pp. 239-250 (1991).
Office Action for U.S. Appl. No. 12/084,575, issued by the USPTO on Aug. 29, 2011.
Doherty et al., "Selectivity for the methoxycarbonylation of ethylene versus CO-ethylene copolymerization with catalysts based on C4-bridged bidentate phosphines and phospholes," Journal of Organometallic Chemistry, vol. 640, pp. 182-196, 2001.
Dörwald, Side Reactions in Organic Synthesis: A Guide to Successful Synthesis Design, Weinheim—Wiley-VCH, pp. ix, 1-16, 2005.
Office Action for European Application No. 07848735.2, issued by the EPO on Sep. 9, 2011.
Office Action for Australian Application No. 2006314268, issued by the Australian Patent Office on Nov. 11, 2010.
Office Action for European Application No. 07824927.3, issued by the EPO on Mar. 30, 2011.
Office Action for GCC Application No. GCC/P/2007/8136 issued by the State Intellectual Property Office of the P.R. China on Nov. 5, 2010.
Office Action for Chinese Application No. 200580011699.0 issued by the State Intellectual Property Office of the P.R. China on Jun. 23, 2011.
Office Action for Japanese Application based on International Application No. PCT/GB2005/000569 issued by the Patent Office of Japan on Jun. 21, 2011.
Office Action for U.S. Appl. No. 12/297,023, issued by the USPTO on Sep. 27, 2011.
Office Action for U.S. Appl. No. 11/990,272, issued by the USPTO on Oct. 28, 2011.
Office Action for U.S. Appl. No. 12/518,320, issued by the USPTO on Dec. 6, 2011.
Office Action for Taiwanese Application No. 094104929 issued by the Intellectual Property Office of Taiwan on Sep. 21, 2011.
Office Action for U.S. Appl. No. 12/084,575, issued by the USPTO on Mar. 19, 2012.
Office Action for U.S. Appl. No. 12/297,023, issued by the USPTO on Apr. 12, 2012.
Andrews et al., "Syntheses, Spectra, and Structures of (Diphosphine)platinum(II) Carbonate Complexes," Inorganic Chemistry, vol. 35, No. 19, pp. 5478-5483, 1996.
Office Action issued in Korean Patent Office on Jan. 12, 2012, English translation.
Office Action for U.S. Appl. No. 11/990,272, issued by the USPTO on May 2, 2012.
Office Action for U.S. Appl. No. 12/517,215, issued by the USPTO on Feb. 27, 2012.
Examination Report issued by the State Intellectual Property Office of the P.R. China in Application No. GCC/P/2007/8136 dated Nov. 5, 2010.
Japanese Notice of Reasons for Rejection issued in Application No. 2008-525618 dated Apr. 3, 2012.
Examiner's First Report issued in Australian Application No. 2007327051 dated May 9, 2012.
Japanese Notice of Reasons for Rejection issued in Application No. 2008-540675 dated May 22, 2012.
Clegg et al, "Highly active and selective catalysts for the production of methyl propanoate via the methoxycarbonylation of ethene," Chem. Commun., pp. 1877-1878 (1999).
United Kingdom Search Report issued in Application No. GB0921876.9 dated Oct. 29, 2010.
International Preliminary Report on Patentability issued in Application No. PCT/GB2010/052093 dated Jun. 28, 2012.
Rucklidge, et al., "Methoxycarbonylation of vinyl acetate catalysed by palladium complexes of bis(ditertiarybutylphosphinomethyl) benzene and related ligands", Chemical Communications, 2005, vol. 9 pp. 1176-1178.
Argouarch, et al., "Synthesis of Some Ferrocene-Based 1,3(phosphanes) with Planar Chirality as the Sole Source of Chirality", European Journal of Organic Chemistry, 2000, vol. 16 pp. 2885-2891.
Gray et al., "The Di-*t*-Butylphosphinyl Directed *ortho* Metalation Group, Synthesis of Hindered Dialkylarylphosphines," Synlett Letters, vol. 4, pp. 422-424 (1998).
Godard, et al., "Systematic Study of the Asymmetric Methoxycarbonylation of Styrene Catalyzed by Palladium Systems Containing Chiral Ferrocenyl Diphosphine Ligands", Helvetica Chimica Acta, 2006 vol. 89(8) pp. 1610-1622.
Ooka et al., "Highly active and selective palladium catalyst for hydroesterification of styrene and vinyl acetate promoted by polymeric sulfonic acids," Chemical Communications, pp. 1173-1175 (2005).
Wang, et al., "Synthesis and Use in Asymmetric Hydrogenations of Solely Planar Chiral 1,2-Disubstituted and 1,2,3-Trisubstituted Ferrocenyl Diphosphines: A Comparative Study", Organometallics, 2007, vol. 26, pp. 3530-3540.
Russian Office Action issued in Application No. 201170142/28 dated Apr. 20, 2012.
United Kingdom Search Report issued in Application No. GB0812297.0 dated Jun. 17, 2009.
International Search Report issued in International Application No. PCT/GB2009/050780 dated Oct. 15, 2009.
Written Opinion of the International Searching Authority issued in International Application No. PCT/GB2009/050780 dated Oct. 15, 2009.

(56) **References Cited**

OTHER PUBLICATIONS

Written Opinion of the International Searching Authority issued in International Application No. PCT/GB2010/052214 dated Mar. 30, 2011.
International Search Report issued in International Application No. PCT/GB2010/052214 dated Mar. 30, 2011.
International Search Report issued in International Application No. PCT/GB2010/052093 dated Apr. 8, 2011.
Written Opinion of the International Searching Authority issued in International Application No. PCT/GB2010/052093 dated Apr. 8, 2011.
Examination Report issued from the State Intellectual Property Office of P.R. China issued in Application No. GCC/P/2007/9585 dated Jan. 20, 2012.
Notice of Reason for Rejection issued from the Japanese Office Action in Japanese Application No. 2006-553662 dated Sep. 25, 2012.
Notice of Reason for Rejection issued from the Japanese Office Action in Japanese Application No. 2008-525618 dated Sep. 25, 2012.
Notice of Reasons for Rejection issued from the Japanese Patent Office in Japanese Application No. 2009-504833 dated Jul. 31, 2012.
Notice of Reexamination issued from the Patent Reexamination Board of State Intellectual Property Office of P.R. China in Chinese Application No. 200580011699.0 dated Jul. 30, 2012.
Office Action issued from the Eurasian Patent Organization issued in Application No. 200970528/28 dated Aug. 15, 2012.
Office Action issued in U.S. Appl. No. 11/990,272 dated Feb. 6, 2013.
First Examination Report issued in Indian Application No. 841/MUMNP/2009 dated Nov. 29, 2012.
Office Action issued in Japanese Application No. 2009-538795 dated Feb. 19, 2013.
Office Action issued in Japanese Application No. 2008-540675 dated Nov. 13, 2012.
Office Action issued in Canadian Application No. 2,626,107 dated Nov. 23, 2012.
Office Action issued in Chinese Application No. 200580011699.0 dated Jan. 14, 2013.
Office Action issued in European Application No. 09 772 854.7 dated Oct. 5, 2012.
Office Action issued in Taiwanese Application No. 096113047 dated Jan. 22, 2013.
Office Action issued in Taiwanese Application No. 095128759 dated Jan. 3, 2013.
Office Action issued in Canadian Application No. 2,618,574 dated Dec. 7, 2012.
Notice of Allowance issued in U.S. Appl. No. 12/297,023 dated Feb. 21, 2013.
Notice of Allowance issued in U.S. Appl. No. 12/297,023 dated Dec. 26, 2012.
Office Action issued in U.S. Appl. No. 13/002,406 dated Mar. 15, 2013.
Office Action issued in Chinese Application No. 200780044657.6 dated Mar. 20, 2013.
Office Action issued in Malaysian Application No. PI20092250 dated Mar. 29, 2013.
Office Action issued in Taiwanese Application No. 096145458 dated Mar. 8, 2013.
Office Action issued in Korean Application No. 10-2008-7006106 dated Apr. 24, 2013.
Office Action issued in Chinese Application No. 200980125824.9 dated Feb. 22, 2013.
Office Action issued in European Application No. 09 772 854.7 dated Apr. 23, 2013.
Office Action issued in Eurasian Application No. 201170142.
Office Action issued in Mexican Application No. MX/a/2008/001974 dated Mar. 11, 2013.
Office Action issued in Taiwanese Application No. 095141340 dated Apr. 12, 2013.
Office Action issued in U.S. Appl. No. 10/589,971 dated Aug. 8, 2013.
White et al., "Basic Energy Sciences Advisory Committee Subpanel Workshop Report," Opportunities for Catalysis in the 21st Century, 2002, pp. 1-47.
Notice of Allowance issued in U.S. Appl. No. 11/990,272 dated Jul. 25, 2013.
Office Action issued in U.S. Appl. No. 13/002,406 dated Aug. 19, 2013.
Office Action issued in Indian Application No. 1366/DELNP/2003 dated Jul. 4, 2013.
Office Action issued in Mexican Application No. MX/a/2010/014404 dated Jun. 25, 2013.
Written Opinion of the Intellectual Property Office of Singapore issued in Application No. 201204384-0 dated Jul. 5, 2013.
Kiss, "Palladium-catalyzed Reppe Carbonylation," Chem. Rev. 2001, 101(11): 3435 (Abstract Only).
Letter Reporting Office Action issued in Australian Application No. 2009265367 dated Aug. 20, 2013.
Office Action issued in Canadian Application No. 2,626,107 dated Aug. 8, 2013.
Office Action issued in Canadian Application No. 2,671,409 dated Aug. 23, 2013.
Office Action issued in Chinese Application No. 200780044657.6 dated Sep. 23, 2013.
Office Action issued in Eurasian Application No. 200801345 dated Jun. 27, 2013.
Office Action issued in Eurasian Application No. 201170142/28 dated Aug. 23, 2013.
Office Action issued in Eurasian Application No. 201290605 dated Aug. 22, 2013.
Office Action issued in Indian Application No. 3292/DELNP/2008 dated Sep. 20, 2013.
Office Action issued in Malaysian Application No. PI2011000006 dated Sep. 30, 2013.
Letter Reporting Office Action issued in Mexican Application No. MX/a/2009/005568 dated Sep. 12, 2013.
Office Action issued in Singapore Application No. SE 2013 01311V dated Aug. 9, 2013.
Office Action issued in Chinese Application No. 200980125824.9 dated Oct. 15, 2013.
Letter Reporting Office Action issued in Mexican Application No. MX/a/2010/014404 dated Nov. 27, 2013/.
Office Action issued in Australian Application No. 2010332501 dated Sep. 5, 2013.
Office Action issued in Eurasian Application No. 201290514/28 dated Oct. 28, 2013.
Office Action issued in European Application No. 10172689.1 dated Dec. 5, 2013.
Office Action issued in European Application No. 10172698.2 dated Dec. 5, 2013.
Office Action issued in Taiwanese Application No. 096145458 dated Oct. 9, 2013.
Office Action issued in Korean Application No. 10-208-7014580 dated Jan. 15, 2014.
Office Action issued in Eurasian Application No. 200970528 dated Nov. 18, 2013.
Office Action issued in Chinese Application No. 201080062848.7 dated Dec. 23, 2013.
Office Action issued in Japanese Application No. 2011-515634 dated Dec. 17, 2013.
Imwinkelried, "Catalytic Asymmetric Hydrogenation in the Manufacture of d-Biotin and Dextromethorphan," NSCS Spring Meeting 97: Industrial Asymmetric Synthesis, Chimia 51 (1997) 300-302.
Lee et al., "improved Catalysts for the Palladium-Catalyzed Synthesis of Oxindoles by Amide α-Arylation, Rate Acceleration, Use of Aryl Chloride Substrates, and a New Carbene Ligand for Asymmetric Transformations," J. Org. Chem, 2001, 66, 3402-3415.
Office Action issued in European Application No. 10803476.6 dated Dec. 20, 2013.
Office Action issued in U.S. Appl. No. 12/517,215 dated Mar. 12, 2014.

(56) **References Cited**

OTHER PUBLICATIONS

Office Action issued in U.S. Appl. No. 10/589,971 dated Mar. 6, 2014.
Notice of Allowance issued in U.S. Appl. No. 13/002,406 dated Apr. 9, 2014.
Office Action issued in U.S. Appl. No. 12/084,575 dated Apr. 25, 2014.
Office Action issued in Taiwanese Patent Application No. 098122672 dated Mar. 6, 2014.
Office Action issued in European Patent Application No. 09772854.7 dated Mar. 11, 2014.
Office Action issued in Mexican Application No. MX/a/2010/014404 dated Mar. 31, 2014.
Office Action issued in Eurasian Patent Application No. 201290605 dated Mar. 12, 2014.
Office Action issued in Chinese Patent Application No. 201080060676.X dated Jan. 27, 2014.
Office Action issued in Malaysia Patent Application No. PI20081580 dated Feb. 14, 2014.
Office Action issued in Japanese Patent Application No. 2013-051058 dated Apr. 8, 2014.
Office Action issued in Mexican Patent Application No. MX/a/2009/005568 dated Mar. 10, 2014.
Office Action issued in Eurasian Patent Application No. 200801345/28 dated Jan. 31, 2014.
Office Action issued in Korean Patent Application No. 10-2009-7012397 dated Jan. 22, 2014.
Office Action issued in Japanese Patent Application No. 2009-538795 dated Jan. 21, 2014.
Office Action issued in Canadian Patent Application No. 2,626,107 dated May 9, 2014.
Office Action issued in Taiwanese Patent Application No. 095141340 dated Mar. 21, 2014.
Office Action issued in Brazilian Patent Application. PI0507805-9 dated Mar. 24, 2014.
Office Action issued in European Patent Application No. 10172689.1 dated May 30, 2014.
Office Action issued in European Patent Application No. 10172698.1 dated May 30, 2014.
Office Action issued in Gulf Cooperation Council Patent Application No. GCC/P/2005/17210 dated Mar. 5, 2014.
Notice of Allowance issued in U.S. Appl. No. 13/520,523 dated Jun. 23, 2014.
Office Action issued in U.S. Appl. No. 12/517,215 dated Jun. 24, 2014.
Notice of Allowance issued in U.S. Appl. No. 13/002,406 dated Jul. 3, 2014.
Office Action issued in Eurasian Application No. 201170142 dated Mar. 7, 2014.
Letter reporting Office Action issued in Thailand Patent Application No. 0701006115 dated Jun. 13, 2014.
Office Action issued in Canadian Patent Application No. 2,671,409 dated May 1, 2014.
Office Action issued in Eurasian Patent Application No. 200970528/28 dated May 28, 2014.
Office Action issued in Japanese Patent Application No. 2009-538795 dated Jun. 27, 2014.
Office Action issued in Japanese Patent Application No. 2012-281722 dated Jun. 3, 2014.
Pugh et al., "Methoxycaronylation versus Hydroacylation of Ethene; Dramatic Influence of the Ligand in Cationic Palladium Catalysis," Adv. Synth. Catal., 2002, vol. 344, No. 8, pp. 837-840.
Office Action issued in Japanese Patent Application No. 2012-281721 dated Jul. 1, 2014.
Office Action issued in Chinese Patent Application No. 201310099739.8 dated May 6, 2014.
Examination Report issued in Gulf Cooperation Council Patent Application No. GCC/P/2005/17210 dated Mar. 5, 2014.
Office Action issued in European Patent Application No. 10172698.2 dated May 30, 2014.
Search Report issued in Brazilian Patent Application No. PI0507805-9 dated Mar. 24, 2014.
Office Action issued in Japanese Patent Application No. 2012-543906 dated Jul. 22, 2014.
Corrected Notice of Allowability issued in U.S. Appl. No. 10/589,971 dated Mar. 24, 2015.
Office Action issued in U.S. Appl. No. 12/517,215 dated Apr. 6, 2015.

# PROCESS FOR THE CARBONYLATION OF ETHYLENICALLY UNSATURATED COMPOUNDS, NOVEL CARBONYLATION LIGANDS AND CATALYST SYSTEMS INCORPORATING SUCH LIGANDS

This application is a continuation of U.S. patent application Ser. No. 13/520,523, filed on Jul. 3, 2012, which is a National Stage of International Application No. PCT/GB2010/052214, filed on Dec. 29, 2010.

The present invention relates to a process for the carbonylation of ethylenically unsaturated compounds, with a co-reactant, particularly alcohol or water to give alkoxy and hydroxy-carbonylation thereof, novel bidentate ligands and novel catalyst systems incorporating such ligands. The carbonylation of ethylenically unsaturated compounds using carbon monoxide in the presence of an alcohol or water and a catalyst system comprising a group 6, 8, 9 or 10 metal, for example, palladium, and a phosphine ligand, for example an alkyl phosphine, cycloalkyl phosphine, aryl phosphine, pyridyl phosphine or bidentate phosphine, has been described in numerous European patents and patent applications, for example EP-A-0055875, EP-A-04489472, EP-A-0106379, EP-A-0235864, EP-A-0274795, EP-A-0499329, EP-A-0386833, EP-A-0441447, EP-A-0489472, EP-A-0282142, EP-A-0227160, EP-A-0495547 and EP-A-0495548. In particular, EP-A-0227160, EP-A-0495547 and EP-A-0495548 disclose that bidentate phosphine ligands provide catalyst systems which enable high reaction rates to be achieved. C3 alkyl bridges between the phosphorus atoms are exemplified in EPO495548 together with tertiary butyl substituents on the phosphorus.

WO96/19434 subsequently disclosed that a particular group of bidentate phosphine compounds with tertiary carbon groups but having an aryl bridge could provide remarkably stable catalysts which require little or no replenishment; that use of such bidentate catalysts leads to reaction rates which are significantly higher than those previously disclosed in EPO495548; that little or no impurities are produced at high conversions; and that the product has a high selectivity for the acid or ester product and gives no polymer.

WO 01/68583 discloses rates for the same process and tertiary carbon substituted ligands as WO 96/19434 when used for higher alkenes and when in the presence of an externally added aprotic solvent.

WO 98/42717 discloses a modification to the bidentate phosphines used in EPO495548 wherein the tertiary carbon groups are utilised by one or both phosphorus atoms being incorporated into an optionally substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group or a derivative thereof in which one or more of the carbon atoms are replaced by heteroatoms ("2-PA" group). Asymmetric ligands are envisaged but not exemplified. The examples include a number of alkoxycarbonylations of ethene, propene and some higher terminal and internal olefins using symmetrical PA groups incorporating each phosphorus and substituting each adjacent carbon in the PA groups so that the carbons joined to the phosphorus are tertiary. There are no examples of the use of secondary or primary carbons joined to the phosphorus. Improved rates and improved yields for carbonylation of internally unsaturated olefins are found when compared to 1,3-bis(di-t-butylphosphino)propane.

WO 03/070370 extends the particular tertiary carbon phosphorus substituent ligands taught in WO 98/42717 to bidentate phosphines having 1, 2 substituted aryl bridges of the type disclosed in WO96/19434.



WO 04/103948 describes both the above types of ligand bridges as useful for butadiene carbonylation and WO 05/082830 describes a selection of WO 04/103948 where the tertiary carbon substituents are different on the respective phosphorus atoms leading to improved reaction rate.

It is known that the use of primary, secondary and aromatic carbon substituents on the bidentate phosphorus ligands lead to no or polymer products in the carbonylation of certain ethylenically unsaturated compounds. The general process for the production of polyketone polymers has been known for many years. EP 121,965, EP 181,014 and EP 213,671 describe processes which involve the use of a bidentate phosphine ligand with a group VIII metal such as palladium and an acid having a pKa of less than 6. U.S. Pat. No. 4,950,703 teaches that a preferred catalyst composition for producing polyketone polymer uses palladium, a suitable acid and 1,3-bis(diphenylphosphine)propane or 1,3-bis[di(2-methyoxyphenyl)phosphino]propane.

For instance U.S. Pat. No. 5,369,074 teaches that such aromatic group substituted ligands as 1,2-bis-(diphenylphosphino)propane and alkyl substituted bidentate ligands joined to the phosphorus via a —$CH_2$ group give a range of molecular weight polyketone polymer products in good yield in the carbonylation of ethylene using carbon monoxide.

It is known from WO01/87899 that ligands with the cyclic groups known as phobanes, for example, 9-phosphabicyclononane, joined to the phosphorus via a secondary carbon and with an alkylene bridge can give good selectivity and non-polymer product in such carbonylation reactions. In WO 05/082830 an asymmetric bidentate phosphine ligand is disclosed having tertiary carbons on one phosphorus and the phobane secondary carbons on the other phosphorus. Unsurprisingly, the reaction still gives a good selectivity to the ester product.

Surprisingly, it has now been found that a certain group of aromatic bridged asymmetric bidentate ligands do not give polymer product using the above types of alkyl and aromatic group substituted bidentate ligands when in combination with tertiary carbon substituents and that these ligands also display improved stability and activity in carbonylation reactions especially in the presence of weaker acids than has hitherto proved advantageous.

According to the first aspect of the present invention there is provided a novel bidentate ligand according to the claims.

Optionally, there may be up to 3 nitrogen atoms in the hydrocarbyl $X^1$ or $X^2$ radical of the ligand of the invention with the closest nitrogen atom being separated from the $Q^2$ atom by 1-3, preferably, 1 or 2, more preferably, 1 carbon atom(s). The nitrogen atom may be substituted by hydrogen, aryl, alkyl or fluoroalkyl. The nitrogen atom may be incorporated into a heterocyclic group which may be saturated, unsaturated or part unsaturated. The unsaturated heterocycle may be aromatic or non-aromatic. The heterocycle may have between 3 and 14 ring atoms, preferably between 5 or 10 ring atoms, most preferably, 5 or 6. The heterocyclic group may have between 1 and 3 nitrogen atoms in the ring, preferably 1 or 2, most preferably, 1. The hydrocarbyl radical may be linear, branched or may form ring structures wherein the nitrogen atom(s) may or may not be incorporated into the ring. These ring structures may be monocyclic or polycyclic, saturated, unsaturated or part unsaturated and if unsaturated may be aromatic or non-aromatic. The cyclic ring structure preferably has between 1 and 3 rings, more preferably 1 or 2 rings, most preferably 1 ring and may be heterocyclic with the at least one nitrogen(s) in the ring structure or non-heterocyclic with the said nitrogen(s) outside the ring structure.

Alternatively, the group $X^1$ may be defined as a univalent radical of up to 30 atoms represented by formula Ib

$$(C^1R^{101}R^{102})_y(C^2R^{101}R^{102}R^{110})_x(NR^{101}R^{102})_a \quad \text{(Ib)}$$

wherein $C^1$ is attached directly to $Q^2$ and at least one further atom selected from $C^2$ and N and y=1;

wherein $R^{101}$ and $R^{102}$ represent optional substituents hydrogen, aryl, alkyl or fluoroalkyl when $C^1$, $C^2$ and/or N have 1 or 2 free substituent sites;

wherein the or each $C^2$ atom is either attached directly to an N atom or indirectly to an N atom via another $C^2$ atom, and x is 0 to 6, preferably, 1 to 4, more preferably, 3 or 4;

wherein the or each N is independently attached to $C^1$ or $C^2$ and a is 1, 2 or 3, preferably, 1;

$R^{110}$ is hydrogen, aryl, alkyl or fluoroalkyl;

wherein, when x is 1 or more, $C^2$ may form a cyclic structure of 3 or more atoms which if x is 1 incorporates N and $C^1$, which if x is 2 incorporates N and/or $C^1$ and if x is 3 optionally incorporates N and/or $C^1$.

Preferably, in the present invention, the pKb of the at least one nitrogen atom measured in dilute aqueous solution at 18° C. is between 6 and 12, more preferably, between 7 and 10, most preferably, 7.5 to 9.5. Typically, where there is more than one nitrogen atom, each nitrogen atom may have a pKb as set out above and in the claims. However, it is not essential for any $2^{nd}$ of further nitrogen to have a pKb between 4 and 14.

Preferably, the carbon directly joined to the $Q^2$ atom in the $X^1$ radical is a non-tertiary carbon atom. Typically, the said carbon is a cyclic, primary or secondary carbon atom, more typically, an aromatic or primary carbon atom, especially an aromatic carbon atom.

Preferably, the group $X^1$ is independently selected from an aziridine, azirine, azetidine, azete, pyrrolidone, pyrrole, pyridine, piperidine, azepane, azepine, azocane, azocine imidazolidine, pyrazolidine, imidazole, benzimidazole, imidazoline, pyrazole, indazole, pyrazoline, pyrazine, pyrimidine, pyridazine, piperazine, hexahydro-pyrimidine, hexahydro-pyridazine, indole, isoindole, quinoline, isoquinoline, quinazoline, benzopyrazine, acridine or benzoquinoline radical.

More preferably, the group $X^1$ is independently selected from the group consisting of an aziridine, azirine, azete, pyrrolidone, pyrrole, pyridine, azepane, azepine, azocane, azocine, imidazolidine, pyrazolidine, benzimidazole, imidazoline, indazole, pyrazoline, hexahydro-pyrimidine, hexahydro-pyridazine, isoindole, quinazoline, benzopyrazine, acridine and benzoquinoline radical.

Advantageously, by introducing the groups $X^1$ and optionally $X^2$ to the $Q^2$ atom it has been found that a catalyst system utilising such ligands in carbonylation reactions has surprisingly improved stability over an equivalent system using tertiary carbon atoms joined to both $Q^1$ and $Q^2$. Typically, the turnover number (TON) (moles of metal/moles of product) and/or rate for the carbonylation reaction, especially, hydroxy- or alkoxy-carbonylation is improved.

$X^1$ in the invention may optionally exclude $CH(R^2)(R^3)$ wherein $R^2$ and $R^3$ represent Het and Het represents azetidinyl, pyrrolidinyl, imidazolyl, indolyl, furanyl, oxazolyl, isoxazolyl, oxadiazolyl, thiazolyl, thiadiazolyl, triazolyl, oxatriazolyl, thiatriazolyl, pyridazinyl, morpholinyl, pyrimidinyl, pyrazinyl, quinolinyl, isoquinolinyl, piperidinyl, pyrazolyl and piperazinyl.

Preferably, the ligands of the invention are utilised in continuous carbonylation reactions but batch reactions, particularly repeat batch reactions will also benefit.

Therefore, according to a second aspect of the present invention there is provided a process for the carbonylation of ethylenically unsaturated compounds according to the claims.

Preferably, in the process of the invention the catalyst system also includes an acid and said ligand is present in at least a 1:1 molar ratio, more preferably, at least a 2:1 molar excess compared to said metal or said metal in said metal compound, and that said acid is present in at least a 1:1 molar ratio, more preferably a greater than 2:1 molar excess compared to said ligand.

According to a third aspect of the present invention there is provided a catalyst system according to claim **15**.

Preferably, in the third aspect, said ligand is present in at least a 1:1 molar ratio, more preferably, at least a 2:1 molar excess compared to said metal or said metal in said metal compound, and that said acid is present in at least a 1:1 molar ratio, more preferably a greater than 2:1 molar excess compared to said ligand.

Suitably, all of components a) to c), when present, of the catalyst system of the present invention can be added in situ to the reaction vessel wherein the carbonylation is to take place. Alternatively, the components a) to c) can be added sequentially in any order to form the catalyst system, or in some specified order, either directly into the vessel or outside the vessel and then added to the vessel. For instance, the acid component c) may first be added to the bidentate ligand component b), to form a protonated ligand, and then the protonated ligand can be added to the metal or compound thereof (component a)) to form the catalyst system. Alternatively, the ligand component b) and metal or compound thereof (component a)) can be mixed to form a chelated metal compound, and the acid (component c)) is then added. Alternatively, any two components can be reacted together to form an intermediate moiety which is then either added to the reaction vessel and the third component added, or is first reacted with the third component and then added to the reaction vessel.

As such, the present invention is directed to a process and catalyst system leading to surprising and unexpected advantages when using the catalyst system in the carbonylation of ethylenically unsaturated compounds in combination with the ligands defined herein, and the alleviation or at least reduction of at least some of the disadvantages of the prior art systems. In particular, the use of a catalyst system of the present invention leads to a potentially more stable system, increased reaction rates, improved turnover numbers in carbonylation reactions of ethylenically unsaturated compounds, potentially improved selectivity, improved conversion and an avoidance of polymerisation.

It will be appreciated by those skilled in the art that the compounds of formula (I) mentioned herein may function as ligands that coordinate with the Group 8, 9 or 10 metal or compound thereof to form the catalytic compounds for use in the invention. Typically, the Group 8, 9 or 10 metal or compound thereof coordinates to the one or more phosphorus, arsenic and/or antimony atoms of the compound of formula I.

Co-Reactant

The ratio (mol/mol) of ethylenically unsaturated compound and co-reactant in the reaction can vary between wide limits and suitably lies in the range of 10:1 to 1:500, preferably, 2:1 to 1:2. However, if the ethylenically unsaturated compound is a gas at the reaction temperature it may be present at lower levels in the liquid phase reaction medium such as at a ratio to co-reactant of 1:20,000 to 1:10 more preferably, 1:10,000 to 1:50, most preferably, 1:5000 to 1:500 The co-reactant of the present invention may be any compound including water having a mobile hydrogen atom, and capable of reacting as a nucleophile with the ethylenically unsaturated compound under catalytic conditions. The chemical nature of the co-reactant determines the type of product formed. Possible co-reactants are carboxylic acids, water, alcohols, ammonia or amines, thiols, or a combination thereof.

If the co-reactant is a carboxylic acid the product is an anhydride. For an alcohol co reactant, the product of the carbonylation is an ester. Similarly, the use of ammonia ($NH_3$) or a primary or secondary amine $R^{81}NH_2$ or $R^{82}R^{83}NH$ will produce an amide, and the use of a thiol $R^{81}SH$ will produce a thioester.

In the above-defined co-reactants, $R^{81}$ $R^{82}$ and/or $R^{83}$ represent alkyl, alkenyl or aryl groups which may be unsubstituted or may be substituted by one or more substituents selected from halo, cyano, nitro, $OR^{19}$, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $SR^{29}$, $C(O)SR^{30}$, $C(S)NR^{27}R^{28}$, aryl or Het, wherein $R^{19}$ to $R^{30}$ are defined herein, and/or be interrupted by one or more oxygen or sulphur atoms, or by silano or dialkylsilicon groups.

If ammonia or amines are employed, a small portion of co-reactants will react with acid present in the reaction to form an amide and water. Therefore, in the case of ammonia or amine-co-reactants, water may be generated in situ.

Preferred amine co-reactants have from 1 to 22, more preferably, 1 to 8 carbon atoms per molecule, and diamine co-reactants preferably have 2 to 22, more preferably 2 to 10 carbon atoms per molecule. The amines can be cyclic, part-cyclic, acyclic, saturated or unsaturated (including aromatic), unsubstituted or substituted by one or more substituents selected from halo, cyano, nitro, $OR^{19}$, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $SR^{29}$, $C(O)SR^{30}$, $C(S)NR^{27}R^{28}$, aryl, alkyl, Het, wherein $R^{19}$ to $R^{30}$ are as defined herein and/or be interrupted by one or more (preferably less than a total of 4) oxygen, nitrogen, sulphur, silicon atoms or by silano or dialkyl silicon groups or mixtures thereof.

The thiol co-reactants can be cyclic, part-cyclic, acyclic, saturated or unsaturated (including aromatic), unsubstituted or substituted by one or more substituents selected from halo, cyano, nitro, $OR^{19}$, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $SR^{29}$, $C(O)SR^{30}$, $C(S)NR^{27}R^{28}$, aryl, alkyl, Het, wherein $R^{19}$ to $R^{30}$ are as defined herein and/or be interrupted by one or more (preferably less than a total of 4) oxygen, nitrogen, sulphur, silicon atoms or by silano or dialkyl silicon groups or mixtures thereof. Preferred thiol co-reactants are aliphatic thiols with 1 to 22, more preferably with 1 to 8 carbon atoms per molecule, and aliphatic di-thiols with 2 to 22, more preferably 2 to 8 carbon atoms per molecule.

If a co-reactant should react with the acid serving as a source of anions, then the amount of the acid to co-reactant should be chosen such that a suitable amount of free acid is still present in the reaction. A large surplus of acid over the co-reactant may be advantageous due to the enhanced reaction rates facilitated by the excess acid.

As mentioned above, the present invention provides a process for the carbonylation of ethylenically unsaturated compounds comprising contacting an ethylenically unsaturated compound with carbon monoxide and a co-reactant. The co-reactant is more preferably an organic molecule having an hydroxyl functional group such as an alkanol or water.

Suitably, as mentioned above, the co-reactant includes an organic molecule having an hydroxyl functional group. Preferably, the organic molecule having a hydroxyl functional group may be branched or linear, cyclic, acyclic, part cyclic or aliphatic and is, typically an alkanol, particularly a $C_1$-$C_{30}$ alkanol, including aryl alcohols, which may be optionally substituted with one or more substituents selected from alkyl, aryl, Het, halo, cyano, nitro, $OR^{19}$, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $C(S)NR^{27}R^{28}$, $SR^{29}$ or $C(O)SR^{30}$ as defined herein. Highly preferred alkanols are $C_1$-$C_8$ alkanols such as methanol, ethanol, propanol, iso-propanol, iso-butanol, t-butyl alcohol, phenol, n-butanol and chlorocapryl alcohol. Although the monoalkanols are most preferred, poly-alkanols, preferably, selected from di-octa ols such as diols, triols, tetra-ols and sugars may also be utilised. Typically, such polyalkanols are selected from 1,2-ethanediol, 1,3-propanediol, glycerol, 1,2,4 butanetriol, 2-(hydroxymethyl)-1,3-propanediol, 1,2,6 trihydroxyhexane, pentaerythritol, 1,1,1 tri(hydroxymethyl)ethane, nannose, sorbase, galactose and other sugars. Preferred sugars include sucrose, fructose and glucose. Especially preferred alkanols are methanol and ethanol. The most preferred alkanol is methanol. The amount of alcohol is not critical. Generally, amounts are used in excess of the amount of substrate to be carbonylated. Thus the alcohol may serve as the reaction solvent as well, although, if desired, separate solvents may also be used.

It will be appreciated that the end product of the reaction is determined at least in part by the source of alkanol used. For instance, use of methanol produces the corresponding methyl ester. If the co-reactant is water the product is the corresponding acid. Accordingly, the invention provides a convenient way of adding the group —C(O)O $C_1$-$C_{30}$ alkyl or aryl across the ethylenically unsaturated bond.

Solvents

Preferably, the reaction of the present invention is carried out in the presence of a suitable solvent. Suitable solvents will be described hereafter. Preferably, the group 8, 9 or 10 metal/metal compound and ligand are added to the solvent(s) and preferably, dissolved therein.

Suitable solvents for use in the present invention include ketones, such as for example methylbutylketone; ethers, such as for example anisole (methyl phenyl ether), 2,5,8-trioxanonane (diglyme), diethyl ether, dimethyl ether, methyl-tert-butylether (MTBE), tetrahydrofuran, diphenylether, diisopropylether and the dimethylether of di-ethylene-glycol; oxanes, such as for example dioxane; esters, such as for example methylacetate, dimethyladipate methyl benzoate, dimethyl phthalate and butyrolactone; amides, such as for example dimethylacetamide, N-methylpyrrolidone and dimethyl formamide; sulfoxides and sulphones, such as for example dimethylsulphoxide, di-isopropylsulphone, sulfolane (tetrahydrothiophene-2,2-dioxide), 2-methylsulfolane, diethyl sulphone, tetrahydrothiophene 1,1-dioxide and 2-methyl-4-ethylsulfolane; aromatic compounds, including halo variants of such compounds e.g. benzene, toluene, ethyl benzene o-xylene, m-xylene, p-xylene, chlorobenzene, o-dichlorobenzene, m-dichlorobenzene: alkanes, including halo variants of such compounds e.g. hexane, heptane, 2,2,3-trimethylpentane, methylene chloride and carbon tetrachloride; nitriles e.g. benzonitrile and acetonitrile.

Very suitable are aprotic solvents having a dielectric constant that is below a value of 50, more preferably 1-30, most preferably, 1-10, especially in the range of 2 to 8, at 298 or 293K and $1\times10^5 Nm^{-2}$. In the context herein, the dielectric constant for a given co-solvent is used in its normal meaning of representing the ratio of the capacity of a condenser with that substance as dielectric to the capacity of the same condenser with a vacuum for dielectric. Values for the dielectric constants of common organic liquids can be found in general reference books, such as the Handbook of Chemistry and Physics, $76^{th}$ edition, edited by David R. Lide et al, and published by CRC press in 1995, and are usually quoted for a temperature of about 20° C. or 25° C., i.e. about 293.15 k or 298.15 K, and atmospheric pressure, i.e. about $1\times10^5 Nm^{-2}$, and can readily be converted to 298.15 K and atmospheric pressure using the conversion factors quoted. If no literature data for a particular compound is available, the dielectric constant may be readily measured using established physicochemical methods.

Measurement of a dielectric constant of a liquid can easily be performed by various sensors, such as immersion probes, flow-through probes, and cup-type probes, attached to various meters, such as those available from the Brookhaven Instruments Corporation of Holtsville, N.Y. (e.g., model BI-870) and the Scientifica Company of Princeton, N.J. (e.g. models 850 and 870). For consistency of comparison, preferably all measurements for a particular filter system are performed at substantially the same sample temperature, e.g., by use of a water bath. Generally, the measured dielectric constant of a substance will increase at lower temperatures and decrease at higher temperatures. The dielectric constants falling within any ranges herein, may be determined in accordance with ASTM D924.

However, if there is doubt as to which technique to use to determine the dielectric constant a Scientifica Model 870 Dielectric Constant Meter with a 1-200 $\in$ range setting should be used.

For example, the dielectric constant of methyl-tert-butyl ether is 4.34 (at 293 K), of dioxane is 2.21 (at 298 K), of toluene is 2.38 (at 298 K), tetrahydrofuran is 7.5 (at 295.2 K) and of acetonitrile is 37.5 (at 298 K). The dielectric values are taken from the handbook of chemistry and physics and the temperature of the measurement is given.

Alternatively, the reaction may proceed in the absence of an aprotic solvent not generated by the reaction itself. In other words, the only aprotic solvent is the reaction product. This aprotic solvent may be solely generated by the reaction itself or, more preferably, is added as a solvent initially and then also produced by the reaction itself.

Alternatively, a protic solvent or a source thereof may be used. The protic solvent may include a carboxylic acid (as defined above) or an alcohol. Suitable protic solvents include the conventional protic solvents known to the person skilled in the art, such as lower alcohols, such as, for example, methanol, ethanol and isopropanol, and primary and secondary amines. Mixtures of the aprotic and protic co-solvents may also be employed both initially and when generated by the reaction itself.

By protic solvent is meant any solvent that carries a donatable hydrogen ion such as those attached to oxygen as in a hydroxyl group or nitrogen as in an amine group. By aprotic solvent is meant a type of solvent which neither donates nor accepts protons.

Metal

For the avoidance of doubt, references to Group 8, 9 or 10 metals herein should be taken to include Groups 8, 9 and 10 in the modern periodic table nomenclature. By the term "Group 8, 9 or 10" we preferably select metals such as Ru, Rh, Os, Ir, Pt and Pd. Preferably, the metals are selected from Ru, Pt and Pd, more preferably, the metal is Pd.

Anion

Suitable compounds of such Group 8, 9 or 10 metals include salts of such metals with, or compounds comprising weakly coordinated anions derived from, nitric acid; sulphuric acid; lower alkanoic (up to $C_{12}$) acids such as acetic acid and propionic acid; sulphonic acids such as methane sulphonic acid, chlorosulphonic acid, fluorosulphonic acid, trifluoromethane sulphonic acid, benzene sulphonic acid, naphthalene sulphonic acid, toluene sulphonic acid, e.g. p-toluene sulphonic acid, t-butyl sulphonic acid, and 2-hydroxypropane sulphonic acid; sulphonated ion exchange resins (including low acid level sulphonic resins) perhalic acid such as perchloric acid; halogenated carboxylic acids such as trichloroacetic acid and trifluoroacetic acid; orthophosphoric acid; phosphonic acids such as benzenephosphonic acid; and acids derived from interactions between Lewis acids and Broensted acids. Other sources which may provide suitable anions include the optionally halogenated tetraphenyl borate derivatives, e.g. perfluorotetraphenyl borate. Additionally, zero valent palladium complexes particularly those with labile ligands, e.g. triphenylphosphine or alkenes such as dibenzylideneacetone or styrene or tri(dibenzylideneacetone)dipalladium may be used.

The above anions may be introduced directly as a compound of the metal but may also be introduced to the catalyst system independently of the metal or metal compound. Preferably, they are introduced as the acid. Preferably, an acid is selected to have a pKa less than 6 measured in dilute aqueous solution at 18° C. The pKa is preferably less than about 5 measured in dilute aqueous solution at 18° C. Particularly preferred acids have a pKa of less than 2 measured in dilute aqueous solution at 18° C. but, in the case of some substrates such as dienes, a pKa of between 2-6 measured in dilute aqueous solution at 18° C. is preferred. Suitable acids and salts may be selected from the acids and salts listed supra.

Accordingly, preferably, the catalyst system of the present invention includes a source of anions preferably derived from one or more acids having a pKa in aqueous solution at 18° C. of less than 6, more preferably, less than 5, most preferably, less than 2.

Addition of such acids to the catalyst system is preferred and provides acidic reaction conditions.

For the avoidance of doubt, references to pKa herein are references to pKa measured in dilute aqueous solution at 18° C. unless indicated otherwise. For the purposes of the invention herein, the pKa may be determined by suitable techniques known to those skilled in the art.

In the carbonylation reaction the quantity of anion present is not critical to the catalytic behaviour of the catalyst system. The molar ratio of anion to Group 8, 9 or 10 metal or compound may be from 1:1 to 10000:1, preferably from 10:1 to 2000:1 and particularly from 100:1 to 1000:1. However, for a weak acid having a pKa in dilute aqueous solution at 18° C. greater than 0, the molar ratio may be higher and from 1:1 to 100,000:1, preferably, 500:1 to 500,000:1, more preferably, 1000:1 to 10,000:1. Where the anion is provided by an acid and salt, the relative proportion of the acid and salt is not critical. Accordingly, if a co-reactant should react with an acid serving as source of anions, then the amount of the acid to co-reactant should be chosen such that a suitable amount of free acid is present.

Advantageously, the ligands of the invention show surprisingly good activity with relatively weak acids having a pKa in dilute aqueous solution at 18° C. greater than 0 and less than 6. For instance, the ligands of the invention show good activity with trifluoroacetic acid and activity with propionic acid. In industrial processes the possibility of activity in the presence of a relatively weak acid will be advantageous due to lower corrosion of plant parts.

Carbonylating Agent and Process Conditions

In the process according to the present invention, the carbon monoxide may be used in pure form or diluted with an inert gas such as nitrogen, carbon dioxide or a noble gas such as argon.

Hydrogen may optionally be added to the carbonylation reaction to improve reaction rate. Suitable levels of hydrogen when utilised may be in the ratio of between 0.1 and 10% vol/vol of the carbon monoxide, more preferably, 1-10% vol/vol of the carbon monoxide, more preferably, 2-5% vol/vol of the carbon monoxide, most preferably 3-5% vol/vol of carbon monoxide.

The molar ratio of the amount of ethylenically unsaturated compound used in the reaction to the amount of solvent is not critical and may vary between wide limits, e.g. from 1:1 to 1000:1 mol/mol. Preferably, the molar ratio of the amount of ethylenically unsaturated compound used in the reaction to the amount of solvent is between 1:2 and 1:500, more preferably, 1:2 to 1:100. For the avoidance of doubt, such solvent includes the reaction product and co-reactant.

The amount of the catalyst of the invention used in the carbonylation reaction is not critical. Good results may be obtained, preferably when the amount of Group 8, 9 or 10 metal is in the range $1\times10^{-7}$ to $10^{-1}$ moles per mole of ethylenically unsaturated compound, more preferably, $1\times10^{-6}$ to $10^{-1}$ moles, most preferably $1\times10^{-6}$ to $10^{-2}$ moles per mole of ethylenically unsaturated compound.

Preferably, the amount of ligand of formula I to ethylenically unsaturated compound is in the range $1\times10^{-6}$ to $10^{-1}$, more preferably, $1\times10^{-5}$ to $10^{-1}$, most preferably, $1\times10^{-5}$ to $10^{-2}$ moles per mole of ethylenically unsaturated compound. Preferably, the amount of catalyst is sufficient to produce product at an acceptable rate commercially.

Preferably, the carbonylation is carried out at temperatures of between −30 to 170° C., more preferably −10° C. to 160° C., most preferably 20° C. to 150° C. An especially preferred temperature is one chosen between 40° C. to 150° C. Alternatively, the carbonylation can be carried out at moderate temperatures, it is particularly advantageous in some circumstances to be able to carry out the reaction at or around room temperature (20° C.)

Preferably, when operating a low temperature carbonylation, the carbonylation is carried out between −30° C. to 49° C., more preferably, −10° C. to 45° C., still more preferably 0° C. to 45° C., most preferably 10° C. to 45° C. Especially preferred is a range of 10 to 35° C.

Preferably, the carbonylation is carried out at a CO partial pressure in the reactor of between $0.01\times10^{5}N\cdot m^{-2}$-$2\times10^{5}N\cdot m^{-2}$, more preferably $0.02\times10^{5}\ N\cdot m^{-2}$-$1\times10^{5}N\cdot m^{-2}$, most preferably $0.05$–$0.5\times10^{5}\ N\cdot m^{-2}$. Especially preferred is a CO partial pressure of 0.1 to $0.3\times10^{5}N\cdot m^{-2}$.

In the continuous carbonylation reaction of the invention, preferably, the ratio of equivalents of bidentate ligand to group 8, 9 or 10 metal is at least 1:1 mol/mol. The ligand may be in excess of metal mol/mol but is especially between 1:1 and 2:1 mol/mol.

Preferably, generally, the mole ratio of ligand to group 8, 9 or 10 metal for a bidentate ligand is between 1:1 and 100:1, more preferably, 1:1 to 50:1, most preferably, 1:1 to 20:1. For a monodentate, tridentate, etc ligand the mole ratio is varied accordingly.

Preferably, the mole ratio of ligand to acid in the reactor for a bidentate ligand and a monoprotic acid is at least 1:2 and may be up to 1:25000. However, typically, for most applications, a range of 1:4 to 1:5000, more typically, 1:10 to 1:2000 is sufficient. For a monodentate, tridentate, etc ligand and/or diprotic, or triprotic etc acid, the mole ratio is varied accordingly.

Preferably, the acid is present in the catalyst system, or precursor thereto, in such quantity that the molar ratio of said acid to said metal is at least 4:1, more preferably from 4:1 to 100000:1, even more preferably 10:1 to 75000:1, yet more preferably 20:1 to 50000:1, yet still more preferably 25:1 to 50000:1, yet still more preferably 30:1 to 50000:1, yet even more preferably 40:1 to 40000:1, still more preferably 100:1 to 25000:1, yet still more preferably 200:1 to 25000:1, most preferably 550:1 to 20000:1, or greater than 2000:1 to 20000:1. Alternatively, the said ratio can be in the range 125:1 to 485:1, more preferably 150:1 to 450:1, even more preferably 175:1 to 425:1, yet even more preferably 200:1 to 400:1, most preferably 225:1 to 375:1.

For a diprotic, triprotic, etc acid, the mole ratio is varied accordingly.

For the avoidance of doubt, the above ratio conditions apply at the start of a batch reaction or during a continuous reaction.

As mentioned, the catalyst system of the present invention may be used homogeneously or heterogeneously. Preferably, the catalyst system is used homogeneously.

Suitably, the catalysts of the invention are prepared in a separate step preceding their use in-situ in the carbonylation reaction.

Conveniently, the process of the invention may be carried out by dissolving the Group 8, 9 or 10 metal or compound thereof as defined herein in a suitable solvent such as one of the alkanols or aprotic solvents previously described or a mixture thereof. A particularly preferred solvent would be the product of the specific carbonylation reaction which may be mixed with other solvents or co-reactants. Subsequently, the admixed metal and solvent may be mixed with a compound of formula I as defined herein.

The carbon monoxide may be used in the presence of other gases which are inert in the reaction. Examples of such gases include hydrogen, nitrogen, carbon dioxide and the noble gases such as argon.

The product of the reaction may be separated from the other components by any suitable means. However, it is an advantage of the present process that significantly fewer by-products are formed thereby reducing the need for further purification after the initial separation of the product as may be evidenced by the generally significantly higher selectivity. A further advantage is that the other components which contain the catalyst system which may be recycled and/or reused in further reactions with minimal supplementation of fresh catalyst.

There is no particular restriction on the duration of the carbonylation except that carbonylation in a timescale which is commercially acceptable is obviously preferred. Carbonylation in a batch reaction may take place in up to 48 hours, more typically, in up to 24 hours and most typically in up to 12 hours. Typically, carbonylation is for at least 5 minutes, more typically, at least 30 minutes, most typically, at least 1 hour. In a continuous reaction such time scales are obviously irrelevant and a continuous reaction can continue as long as the TON is commercially acceptable before catalyst requires replenishment. Significantly, in the present invention, this time scale to replenishment can be increased.

The catalyst system of the present invention is preferably constituted in the liquid phase which may be formed by one or more of the reactants or by the use of one or more solvents as defined herein.

Ethylenically Unsaturated Compounds

Suitably, the process of the invention may be used to catalyse the carbonylation of ethylenically unsaturated compounds in the presence of carbon monoxide and a co-reactant, having a mobile hydrogen atom, and, optionally, a source of anions. The ligands of the invention yield a surprisingly high TON in carbonylation, particularly, monocarbonylation reactions. Consequently, the commercial viability of a carbonylation process will be increased by employing the process of the invention.

Advantageously, use of the catalyst system of the present invention in the carbonylation of ethylenically unsaturated compounds etc also gives good rates especially for alkoxycarbonylation.

By monocarbonylation is meant the combination of an ethylenically unsaturated moiety and a single carbon monoxide molecule to produce a new insertion carbonylation end product without further insertion of a second or further ethylenically unsaturated compound. Accordingly, the end product of a monocarbonylation reaction cannot be a polymer or oligomer which are both derived from multiple carbon monoxide and ethylenically unsaturated compound insertions into a growing molecule. However, if there is more than one double bond in the ethylenically unsaturated compound then each double bond may combine with a single carbon monoxide molecule to form a new species but further insertion of a second or further ethylenically unsaturated compound will not take place and monocarbonylation should be understood accordingly.

References to ethylenically unsaturated compounds herein should be taken to include any one or more unsaturated C—C bond(s) in a compound such as those found in alkenes, alkynes, conjugated and unconjugated dienes, functional alkenes etc.

Suitable ethylenically unsaturated compounds for the invention are ethylenically unsaturated compounds having from 2 to 50 carbon atoms per molecule, or mixtures thereof. Suitable ethylenically unsaturated compounds may have one or more isolated or conjugated unsaturated bonds per molecule. Preferred are compounds having from 2 to 20 carbon atoms, or mixtures thereof, yet more preferred are compounds having at most 18 carbon atoms, yet more at most 16 carbon atoms, again more preferred compounds have at most 10 carbon atoms. The ethylenically unsaturated compound may further comprise functional groups or heteroatoms, such as nitrogen, sulphur or oxide. Examples include carboxylic acids, esters or nitriles as functional groups. In a preferred group of processes, the ethylenically unsaturated compound is an olefin or a mixture of olefins. Suitable ethylenically unsaturated compounds include acetylene, methyl acetylene, propyl acetylene, 1,3-butadiene, ethylene, propylene, butylene, isobutylene, pentenes, pentene nitriles, alkyl pentenoates such as methyl 3-pentenoates, pentene acids (such as 2- and 3-pentenoic acid), heptenes, vinyl esters such as vinyl acetate, octenes, dodecenes.

Particularly preferred ethylenically unsaturated compounds are ethylene, vinyl acetate, 1,3-butadiene, alkyl pentenoates, pentenenitriles, pentene acids (such as 3 pentenoic acid), acetylene, heptenes, butylene, octenes, dodecenes and propylene.

Especially preferred ethylenically unsaturated compounds are ethylene, propylene, heptenes, octenes, dodecenes, vinyl acetate, 1,3-butadiene and pentene nitriles, most especially preferred is ethylene.

Still further, it is possible to carbonylate mixtures of alkenes containing internal double bonds and/or branched alkenes with saturated hydrocarbons. Examples are raffinate 1, raffinate 2 and other mixed streams derived from a cracker, or mixed streams derived from alkene dimerisation (butene dimerisation is one specific example) and Fischer Tropsch reactions.

References to vinyl esters herein include references to substituted or unsubstituted vinyl ester of formula V:

$$R^{66}—C(O)OCR^{63}═CR^{64}R^{65} \qquad V$$

wherein $R^{66}$ may be selected from hydrogen, alkyl, aryl, Het, halo, cyano, nitro, $OR^{19}$, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $C(S)R^{27}R^{28}$, $SR^{29}$, $C(O)SR^{30}$ wherein $R^{19}$-$R^{30}$ are as defined herein.

Preferably, $R^{66}$ is selected from hydrogen, alkyl, phenyl or alkylphenyl, more preferably, hydrogen, phenyl, $C_1$-$C_6$ alkylphenyl or $C_1$-$C_6$ alkyl, such as methyl, ethyl, propyl, butyl, pentyl and hexyl, even more preferably, $C_1$-$C_6$ alkyl, especially methyl.

Preferably, $R^{63}$-$R^{65}$ each independently represents hydrogen, alkyl, aryl or Het as defined herein. Most preferably, $R^{63}$-$R^{65}$ independently represents hydrogen.

When the ethylenically unsaturated compound is a conjugated diene it contains at least two conjugated double bonds in the molecule. By conjugation is meant that the location of the 7c-orbital is such that it can overlap other orbitals in the molecule. Thus, the effects of compounds with at least two conjugated double bonds are often different in several ways from those of compounds with no conjugated bonds.

The conjugated diene preferably is a conjugated diene having from 4 to 22, more preferably from 4 to 10 carbon atoms per molecule. The conjugated diene can be substituted with one or more further substituents selected from aryl, alkyl, hetero (preferably oxygen), Het, halo, cyano, nitro, $—OR^{19}$, $—OC(O)R^{20}$, $—C(O)R^{21}$, $—C(O)OR^{22}$, $—N(R^{23})R^{24}$, $—C(O)N(R^{25})R^{26}$, $—SR^{29}$, $—C(O)SR^{30}$, $—C(S)N(R^{27})R^{28}$ or $—CF_3$ wherein $R^{19}$-$R^{28}$ are as defined herein or non-substituted. Most preferably, the conjugated diene is selected from conjugated pentadienes, conjugated hexadienes, cyclopentadiene and cyclohexadiene all of which may be substituted as set out above or unsubstituted. Especially preferred are 1,3-butadiene and 2-methyl-1,3-butadiene and most especially preferred is non-substituted 1,3-butadiene.

Bridging Group R

Preferably, the group R which is joined to A and B, as defined, on available adjacent atoms of the at least one aromatic ring, is also substituted with one or more substituent(s) $Y^x$ on one or more further aromatic cyclic atom(s) of the aromatic structure. Preferably, the substituent(s) $Y^x$ on the aromatic structure has a total ${}^{x=1-n}\Sigma tY^x$ of atoms other than hydrogen such that ${}^{X=1-n}\Sigma tY^x$ is ≥4, where n is the total number of substituent(s) $Y^x$ and $tY^x$ represents the total number of atoms other than hydrogen on a particular substituent $Y^x$.

Typically, when there is more than one substituent $Y^x$ hereinafter also referred to as simply Y, any two may be located on the same or different aromatic cyclic atoms of the aromatic structure. Preferably, there are ≤10 Y groups ie n is 1 to 10, more preferably there are 1-6 Y groups, most preferably 1-4 Y groups on the aromatic structure and, especially, 1, 2 or 3 substituent Y groups on the aromatic structure. The substituted cyclic aromatic atoms may be carbon or hetero but are preferably carbon.

Preferably, ${}^{X=1-n}\Sigma tY^x$ is between 4-100, more preferably, 4-60, most preferably, 4-20, especially 4-12.

Preferably, when there is one substituent Y, Y represents a group which is at least as sterically hindering as phenyl and when there are two or more substituents Y they are each as sterically hindering as phenyl and/or combine to form a group which is more sterically hindering than phenyl.

By sterically hindering herein, whether in the context of the groups $R^4$-$R^{12}$ described hereinafter or the substituent Y, we mean the term as readily understood by those skilled in the art but for the avoidance of any doubt, the term more sterically hindering than phenyl can be taken to mean having a lower degree of substitution (DS) than $PH_2Ph$ when $PH_2Y$ (representing the group Y) is reacted with $Ni(0)(CO)_4$ in eightfold excess according to the conditions below. Similarly, references to more sterically hindering than t-butyl can be taken as references to DS values compared with $PH_2$t-Bu etc. If two Y groups are being compared and $PHY^1$ is not more sterically hindered than the reference then $PHY^1Y^2$ should be compared with the reference. Similarly, if three Y groups are being compared and $PHY^1$ or $PHY^1Y^2$ are not already determined to be more sterically hindered than the standard then $PY^1Y^2Y^3$ should be compared. If there are more than three Y groups they should be taken to be more sterically hindered than t-butyl.

Steric hindrance in the context of the invention herein is discussed on page 14 et seq of "Homogenous Transition Metal Catalysis—A Gentle Art", by C. Masters, published by Chapman and Hall 1981. Tolman ("Phosphorus Ligand Exchange Equilibria on Zerovalent Nickel. A Dominant Role for Steric Effects", Journal of American Chemical Society, 92, 1970, 2956-2965) has concluded that the property of the ligands which primarily determines the stability of the Ni(O) complexes is their size rather than their electronic character.

To determine the relative steric hindrance of a group Y the method of Tolman to determine DS may be used on the phosphorus analogue of the group to be determined as set out above.

Toluene solutions of $Ni(CO)_4$ were treated with an eight-fold excess of phosphorus ligand; substitution of CO by ligand was followed by means of the carbonyl stretching vibrations in the infrared spectrum. The solutions were equilibrated by heating in sealed tubes for 64 hr at 100°. Further heating at 100° for an additional 74 hrs did not significantly change the spectra. The frequencies and intensities of the carbonyl stretching bands in the spectra of the equilibriated solutions are then determined. The degree of substitution can be estimated semi-quantitatively from the relative intensities and the assumption that the extinction coefficients of the bands are all of the same order of magnitude. For example, in the case of $P(C_6H_{11})_3$ the $A_1$ band of $Ni(CO)_3L$ and the $B_1$ band of $Ni(CO)_2L_2$ are of about the same intensity, so that the degree of substitution is estimated at 1.5. If this experiment fails to distinguish the respective ligands then the diphenyl phosphorus $PPh_2H$ or di-t-butyl phosphorus should be compared to the $PY_2H$ equivalent as the case may be. Still further, if this also fails to distinguish the ligands then the $PPh_3$ or $P(^tBu)_3$ ligand should be compared to $PY_3$, as the case may be. Such further experimentation may be required with small ligands which fully substitute the $Ni(CO)_4$ complex.

The group Y may also be defined by reference to its cone angle which can be defined in the context of the invention as the apex angle of a cylindrical cone centred at the midpoint of the aromatic ring. By midpoint is meant a point in the plane of the ring which is equidistant from the cyclic ring atoms.

Preferably, the cone angle of the at least one group Y or the sum of the cone angles of two or more Y groups is at least 10°, more preferably, at least 20°, most preferably, at least 30°. Cone angle should be measured according to the method of Tolman (C. A. Tolman Chem. Rev. 77, (1977), 313-348) except that the apex angle of the cone is now centred at the midpoint of the aromatic ring. This modified use of Tolman cone angles has been used in other systems to measure steric effects such as those in cyclopentadienyl zirconium ethene polymerisation catalysts (Journal of Molecular Catalysis: Chemical 188, (2002), 105-113).

The substituents Y are selected to be of the appropriate size to provide steric hindrance with respect to the active site between the $Q^1$ and $Q^2$ atoms. However, it is not known whether the substituent is preventing the metal leaving, directing its incoming pathway, generally providing a more stable catalytic confirmation, or acting otherwise.

A particularly preferred ligand is found when Y represents —$SR^{40}R^{41}R^{42}$ wherein S represents Si, C, N, S, O or aryl and $R^{40}R^{41}R^{42}$ are as defined hereinafter. Preferably each Y and/or combination of two or more Y groups is at least as sterically hindering as t-butyl.

More preferably, when there is only one substituent Y, it is at least as sterically hindering as t-butyl whereas where there are two or more substituents Y, they are each at least as sterically hindering as phenyl and at least as sterically hindering as t-butyl if considered as a single group.

Preferably, when S is aryl, $R^{40}$, $R^{41}$ and $R^{42}$ are independently hydrogen, alkyl, —$BQ^3$-$X^3(X^4)$ (wherein B, $X^3$ and $X^4$ are as defined herein and $Q^3$ is defined as $Q^1$ or $Q^2$ above), phosphorus, aryl, arylene, alkaryl, arylenalkyl, alkenyl, alkynyl, het, hetero, halo, cyano, nitro, —$OR^{19}$, —$OC(O)R^{20}$, —$C(O)R^{21}$, —$C(O)OR^{22}$, —$N(R^{23})R^{24}$, —$C(O)N(R^{25})R^{26}$, —$SR^{29}$, —$C(O)SR^{30}$, —$C(S)N(R^{27})R^{28}$, —$CF_3$, —$SiR^{71}R^{72}R^{73}$ or alkylphosphorus.

$R^{19}$-$R^{30}$ referred to herein may independently be generally selected from hydrogen, unsubstituted or substituted aryl or unsubstituted or substituted alkyl, in addition $R^{21}$ may be nitro, halo, amino or thio.

Preferably, when S is Si, C, N, S or O, $R^{40}$, $R^{41}$ and $R^{42}$ are independently hydrogen, alkyl, phosphorus, aryl, arylene, alkaryl, aralkyl, arylenalkyl, alkenyl, alkynyl, het, hetero, halo, cyano, nitro, —$OR^{19}$, —$OC(O)R^{20}$, —$C(O)R^{21}$, —$C(O)OR^{22}$, —$N(R^{23})R^{24}$, —$C(O)N(R^{25})R^{26}$, —$SR^{29}$, —$C(O)SR^{30}$, —$C(S)N(R^{27})R^{28}$, —$CF_3$, —$SiR^{71}R^{72}R^{73}$, or alkylphosphorus wherein at least one of $R^{40}$-$R^{42}$ is not hydrogen and wherein $R^{19}$-$R^{30}$ are as defined herein, and $R^{71}$-$R^{73}$ are defined as $R^{40}$-$R^{42}$ but are preferably $C_1$-$C_4$ alkyl or phenyl.

Preferably, S is Si, C or aryl. However, N, S or O may also be preferred as one or more of the Y groups in combined or in the case of multiple Y groups. For the avoidance of doubt, as oxygen or sulphur can be bivalent, $R^{40}$-$R^{42}$ can also be lone pairs.

Preferably, alternatively or in addition to group Y, the aromatic structure may be unsubstituted or, when possible be further substituted with groups selected from Y (on the non-aromatic cyclic atoms), alkyl, aryl, arylene, alkaryl, aralkyl, arylenalkyl, alkenyl, alkynyl, het, hetero, halo, cyano, nitro, —$OR^{19}$, —$OC(O)R^{20}$, —$C(O)R^{21}$, —$C(O)OR^{22}$, —$N(R^{23})R^{24}$, —$C(O)N(R^{25})R^{26}$, —$SR^{29}$, —$C(O)SR^{30}$, —$C(S)N(R^{27})R^{28}$, —$CF_3$, —$SiR^{71}R^{72}R^{73}$, or alkylphosphorus wherein $R^{19}$-$R^{30}$ are as defined herein and in the case of Y or a group fulfilling the definition of Y of the first aspect the attachment is to a non-cyclic aromatic atom of the aromatic structure; and $R^{71}$-$R^{73}$ are defined as $R^{40}$-$R^{42}$ but are preferably $C_1$-$C_4$ alkyl or phenyl. In addition, the at least one aromatic ring can be part of a metallocene complex, for instance when R is a cyclopentadienyl or indenyl anion it may form part of a metal complex such as ferrocenyl, ruthenocyl, molybdenocenyl or indenyl equivalents.

Such complexes should be considered as aromatic structures within the context of the present invention so that, when they include more than one aromatic ring, the substituent(s) $Y^x$ may be on the same aromatic ring as that to which the $Q^1$ and $Q^2$ atoms are linked or a further aromatic ring of the structure. For instance, in the case of a metallocene, the substituent $Y^x$ may be on any one or more rings of the metallocene structure and this may be the same or a different ring to which $Q^1$ and $Q^2$ are linked.

Suitable metallocene type ligands which may be substituted with a group Y as defined herein will be known to the skilled person and are extensively defined in WO 04/024322. A particularly preferred Y substituent for such aromatic anions is when S is Si.

In general, however, when S is aryl, the aryl may be further unsubstituted or substituted with, in addition to $R^{40}$, $R^{41}$, $R^{42}$, any of the further substituents defined for the aromatic structure above.

More preferred Y substituents in the present invention may be selected from t-alkyl or t-alkyl,aryl such as -t-butyl or 2-phenylprop-2-yl, —$SiMe_3$, -phenyl, alkylphenyl-, phenylalkyl- or phosphinoalkyl—such as phosphinomethyl.

Preferably, when S is Si or C and one or more of $R^{40}$-$R^{42}$ are hydrogen, at least one of $R^{40}$-$R^{42}$ should be sufficiently bulky to give the required steric hindrance and such groups are preferably phosphorus, phosphinoalkyl-, a tertiary carbon bearing group such as -t-butyl, -aryl, -alkaryl, -aralkyl or tertiary silyl.

Preferably, whether Y is present or not, the hydrocarbyl aromatic structure has, including substituents, from 5 up to 70 cyclic atoms, more preferably, 5 to 40 cyclic atoms, most preferably, 5-22 cyclic atoms, especially 5 or 6 cyclic atoms, if not a metallocene complex.

Preferably, the hydrocarbyl aromatic structure may be monocyclic or polycyclic. The cyclic aromatic atoms may be carbon or hetero, wherein references to hetero herein are references to sulphur, oxygen and/or nitrogen. However, it is preferred that the $Q^1$ and $Q^2$ atoms are linked to available adjacent cyclic carbon atoms of the at least one aromatic ring. Typically, when the cyclic hydrocarbyl structure is polycyclic it is preferably bicyclic or tricyclic. The further cycles in the aromatic structure may or may not themselves be aromatic and aromatic structure should be understood accordingly. A non-aromatic cyclic ring(s) as defined herein may include unsaturated bonds. By cyclic atom is meant an atom which forms part of a cyclic skeleton.

Preferably, the bridging group —R, whether further substituted or otherwise preferably comprises less than 200 atoms, more preferably, less than 150 atoms, more preferably, less than 100 atoms.

By the term one further aromatic cyclic atom of the aromatic structure is meant any further aromatic cyclic atom in the aromatic structure which is not an available adjacent cyclic atom of the at least one aromatic ring to which the $Q^1$ or $Q^2$ atoms are linked, via the linking group.

Preferably, the immediately adjacent cyclic atoms on either side of the said available adjacent cyclic atoms are preferably not substituted. As an example, an aromatic phenyl ring joined to a $Q^1$ atom via position 1 on the ring and joined to a $Q^2$ atom via position 2 on the ring has preferably one or more said further aromatic cyclic atoms substituted at ring position 4 and/or 5 and the two immediately adjacent cyclic atoms to the said available adjacent cyclic atoms not substituted at positions 3 and 6. However, this is only a preferred substituent arrangement and substitution at ring positions 3 and 6, for example, is possible.

The term aromatic ring means that the at least one ring to which the $Q^1$ and $Q^2$ atom are linked via B & A respectively is aromatic, and aromatic should preferably be interpreted broadly to include not only a phenyl, cyclopentadienyl anion, pyrollyl, pyridinyl, type structures but other rings with aromaticity such as that found in any ring with delocalised Pi electrons able to move freely in the said ring.

Preferred aromatic rings have 5 or 6 atoms in the ring but rings with 4n+2 pi electrons are also possible such as [14] annulene, [18] annulene, etc

The hydrocarbyl aromatic structure R may be selected from benzene-1,2 diyl, ferrocene-1,2-diyl, naphthalene-2,3-diyl, 4 or 5 methyl benzene-1,2-diyl, 1'-methyl ferrocene-1,2-diyl, 4 and/or 5 t-alkylbenzene-1,2-diyl, 4,5-diphenyl-benzene-1,2-diyl, 4 and/or 5-phenyl-benzene-1,2-diyl, 4,5-di-t-butyl-benzene-1,2-diyl, 4 or 5-t-butylbenzene-1,2-diyl, 2, 3, 4 and/or 5 t-alkyl-naphthalene-8,9-diyl, 1H-inden-5,6-diyl, 1, 2 and/or 3 methyl-1H-inden-5,6-diyl, 4,7 methano-1H-indene-1,2-diyl, 1, 2 and/or 3-dimethyl-1H-inden 5,6-diyls, 1,3-bis(trimethylsilyl)-isobenzofuran-5,6-diyl, 4-(trimethylsilyl)benzene-1,2 diyl, 4-phosphinomethyl benzene-1,2 diyl, 4-(2'-phenylprop-2'-yl)benzene 1,2 diyl, 4-dimethylsilylbenzene-1,2diyl, 4-di-t-butyl, methylsilyl benzene-1,2diyl, 4-(t-butyldimethylsilyl)-benzene-1,2diyl, 4-t-butylsilyl-benzene-1,2diyl, 4-(tri-t-butylsilyl)-benzene-1,2diyl, 4-(2'-tert-butylprop-2'-yl)benzene-1,2 diyl, 4-(2',2',3',4',4' pentamethyl-pent-3'-yl)-benzene-1,2diyl, 4-(2',2',4',4'-tetramethyl, 3'-t-butyl-pent-3'-yl)-benzene-1,2 diyl, 4-(or 1')$_t$-alkylferrocene-1,2-diyl, 4',5-diphenyl-ferrocene-1,2-diyl, 1')phenyl-ferrocene-1,2-diyl, 4,5-di-t-butyl-ferrocene-1,2-diyl, 4-(or 1')$_t$-butylferrocene-1,2-diyl, 4-(or 1') (trimethylsilyl)ferrocene-1,2 diyl, 4-(or 1')phosphinomethyl ferrocene-1,2 diyl, 4-(or 1')(2'-phenylprop-2'-yl)ferrocene-1,2 diyl, 4-(or 1')dimethylsilylferrocene-1,2diyl, 4-(or 1')di-t-butyl, methylsilyl ferrocene-1,2diyl, 4-(or 1')(t-butyldimethylsilyl)-ferrocene-1,2diyl, 4-(or 1')$_t$-butylsilyl-ferrocene-1,2diyl, 4-(or 1')(tri-t-butylsilyl)-ferrocene-1,2diyl, 4-(or 1')(2'-tert-butylprop-2'-yl)ferrocene-1,2 diyl, 4-(or 1')(2',2',3',4',4' pentamethyl-pent-3'-yl)-ferrocene-1,2diyl, 4-(or 1')(2',2',4',4'-tetramethyl, 3'-t-butyl-pent-3'-yl)-ferrocene-1,2 diyl.

In the structures herein, where there is more than one stereisomeric form possible, all such stereoisomers are intended.

As mentioned above, in some embodiments, there may be two or more of said Y and/or non-Y substituents on further aromatic cyclic atoms of the aromatic structure. Optionally, the said two or more substituents may, especially when themselves on neighbouring cyclic aromatic atoms, combine to form a further ring structure such as a cycloaliphatic ring structure.

Such cycloaliphatic ring structures may be saturated or unsaturated, bridged or unbridged, substituted with alkyl, Y groups as defined herein, aryl, arylene, alkaryl, aralkyl, arylenalkyl, alkenyl, alkynyl, het, hetero, halo, cyano, nitro, —$OR^{19}$, —$OC(O)R^{20}$, —$C(O)R^{21}$, —$C(O)OR^{22}$, —$N(R^{23})R^{24}$, $C(O)N(R^{25})R^{26}$, —$SR^{29}$, —$C(O)SR^{30}$, —$C(S)N(R^{27})R^{28}$, —$CF_3$, —$SiR^{71}R^{72}R^{73}$, or phosphinoalkyl wherein, when present, at least one of $R^{40}$-$R^{42}$ is not hydrogen and wherein $R^{19}$-$R^{20}$ are as defined herein; and $R^{71}$-$R^{73}$ are defined as $R^{40}$-$R^{42}$ but are preferably $C_1$-$C_4$ alkyl or phenyl and/or be interrupted by one or more (preferably less than a total of 4) oxygen, nitrogen, sulphur, silicon atoms or by silano or dialkyl silicon groups or mixtures thereof.

Examples of such structures include piperidine, pyridine, morpholine, cyclohexane, cycloheptane, cyclooctane, cyclononane, furan, dioxane, alkyl substituted DIOP, 2-alkyl substituted 1,3 dioxane, cyclopentanone, cyclohexanone, cyclopentene, cyclohexene, cyclohexadiene, 1,4 dithiane, piperizine, pyrollidine, thiomorpholine, cyclohexenone, bicyclo[4.2.0]octane, bicyclo[4.3.0]nonane, adamantane, tetrahydropyran, dihydropyran, tetrahydrothiopyran, tetrahydro-furan-2-one, delta valerolactone, gamma-butyrolactone, glutaric anhydride, dihydroimidazole, triazacyclononane, triazacyclodecane, thiazolidine, hexahydro-1H-indene (5,6 diyl), octahydro-4,7 methano-indene (1,2 diyl) and tetrahydro-1H-indene (5,6 diyl) all of which may be unsubstituted or substituted as defined for aryl herein.

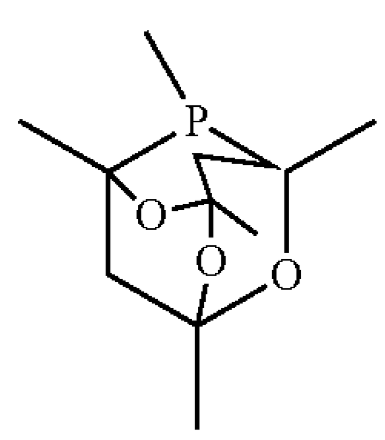
However, whether forming combined groups or otherwise, it is preferred that the immediate adjacent aromatic cyclic atoms, on either side of the said available adjacent cyclic atoms to which $Q^1$ and $Q^2$ are linked, via the said linking group, are un-substituted and preferable substitution is elsewhere on the at least one aromatic ring or elsewhere in the aromatic structure when the aromatic structure comprises more than one aromatic ring and the preferred position of combined Y substituents should be understood accordingly.

Specific but non-limiting examples of unsubstituted and substituted aromatic bridged bidentate ligands within this invention are set out in the claims.

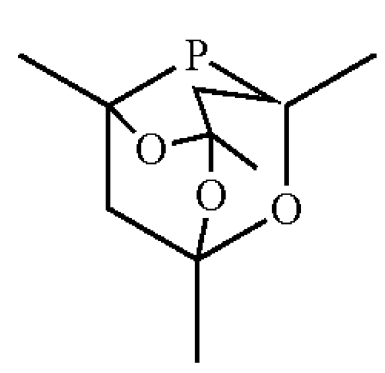
In the said lists of ligands the term "phosphinomethyl-adamantyl" means any one of the following groups 2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl, 2-phosphinomethyl-1,3,5-trimethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl 2-phosphinomethyl-1,3,5,7-tetra(trifluoromethyl)-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl, 2-phosphinomethyl-perfluoro-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo{3.3.1.1[3.7]}-decyl or 2-phosphinomethyl-1,3,5-tri(trifluoromethyl)-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl.

In the said lists of ligands the term "phospha-adamantyl" means any one of the following groups 2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl, 2-phospha-1,3,5-trimethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl, 2-phospha-1,3,5,7-tetra(trifluoromethyl)-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl, perfluoro(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo{3.3.1.1[3.7]}-decyl or 2-phospha-1,3,5-tri(trifluoromethyl)-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl.

For avoidance of doubt the structure of 2-phosphinomethyl-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl etc is as follows: —

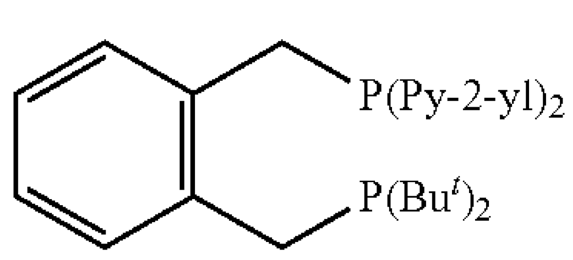



Similarly, the structure of 2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo-{3.3.1.1[3.7]}decyl is as follows: —

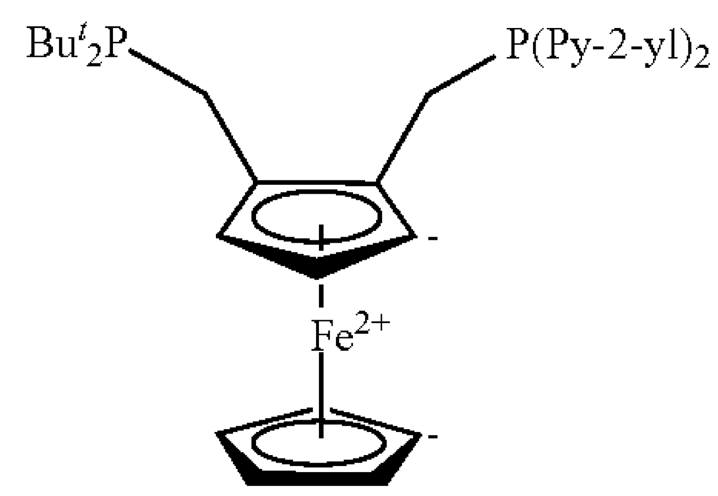



It will be appreciated that in all cases the phosphorus is attached to two tertiary carbon atoms in the phospha-adamantyl skeleton.

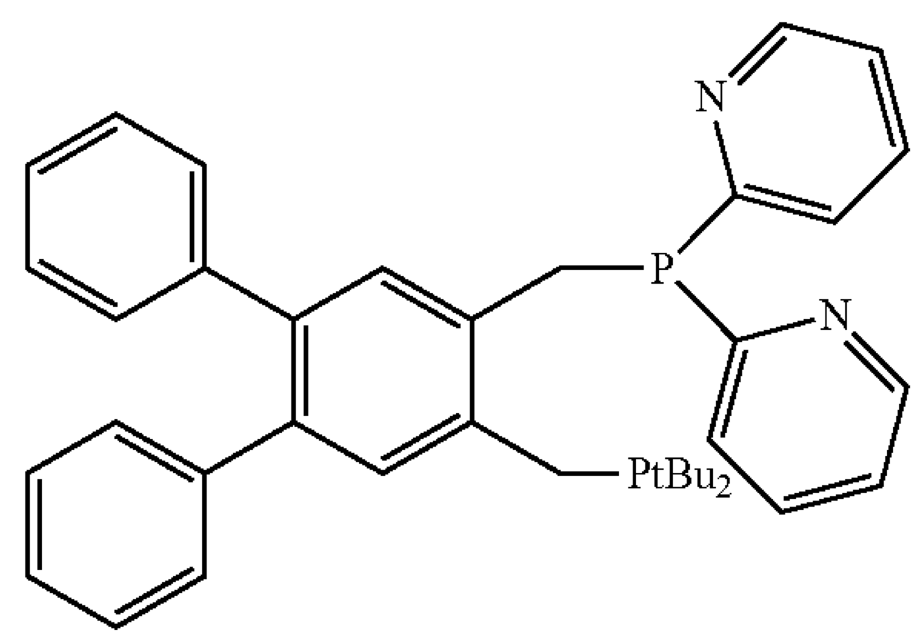
Selected structures of ligands of the invention include: —



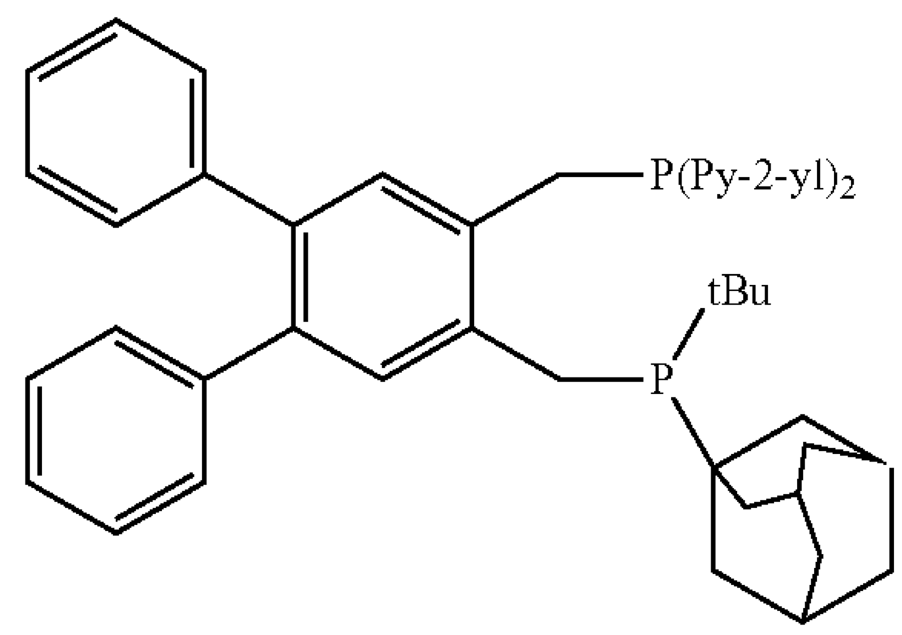

1-(di-tert-butylphosphinomethyl)-2-(di-pyridin-2-ylphosphinomethyl)benzene




1-(di-tert-butylphosphinomethyl)-2-(di-pyridin-2-ylphosphinomethyl)ferrocene,

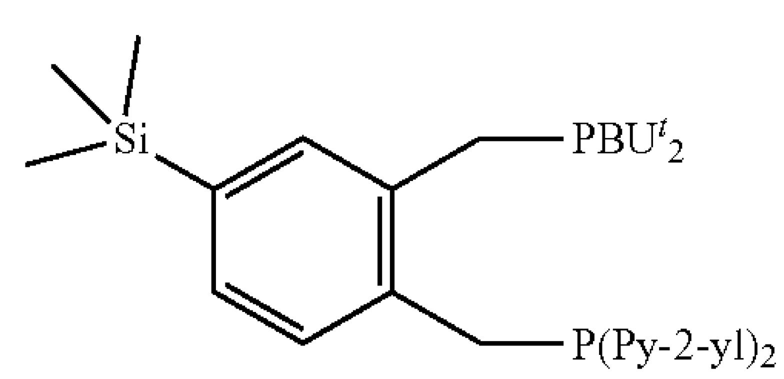



1-(di-t-butylphosphinomethyl)-2-(di-pyridin-2-ylphosphinomethyl)-4,5-diphenyl benzene;

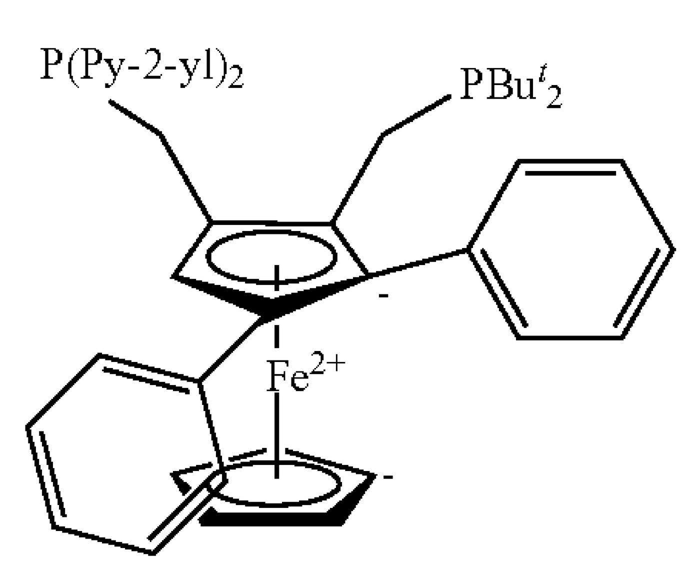



wherein Py-2-yl represents pyridine-2-yl

1-(P,P adamantyl, t-butyl phosphinomethyl)-2-(di-pyridin-2-ylphosphinomethyl)-4,5-diphenylbenzene;




1-(di-pyridin-2-ylphosphinomethyl)-2-(di-tert-butylphosphino)-4-(trimethylsilyl)benzene




1-(di-t-butylphosphinomethyl)-2-(di-pyridin-2-ylphosphinomethyl)-4,5-diphenyl ferrocene;

In the above example structures of ligands one or more of the $X^3$-$X^4$ tertiary carbon bearing groups, t-butyl, attached to the $Q^1$ and/or $Q^2$ group phosphorus may be replaced by a suitable alternative. Preferred alternatives are adamantyl, 1,3 dimethyl adamantyl, congressyl, norbornyl or 1-norbondienyl, or $X^3$ and $X^4$ together form together with the phosphorus a 2-phospha-tricyclo[3.3.1.1{3,7}decyl group such as 2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxadamantyl or 2-phospha-1,3,5-trimethyl-6,9,10-trioxadamantyl. In most embodiments, it is preferred that the univalent $X^1/X^2$ groups and $X^3/X^4$ groups are the same but it may also be advantageous to use different groups to produce further asymmetry around the active site in these selected ligands and generally in this invention.

Similarly, one of the linking groups A or B may be absent so that only A or B is methylene and the phosphorus atom not connected to the methylene group is connected directly to the ring carbon giving a 3 carbon bridge between the phosphorus atoms.

Substituents $X^{2-4}$

Subject to the restrictions defined in the claims and the preferred situation where $X^2$ is the same as $X^1$, the substituents $X^{2-4}$, particularly $X^3$ and $X^4$ may represent various groups. For instance, the group $X^2$ may represent $CH(R^4)(R^5)$, $X^3$ may represent $CR^7(R^8)(R^9)$ and $X^4$ may represent $CR^{10}(R^{11})(R^{12})$, wherein $R^4$ to $R^5$ represent hydrogen, alkyl, aryl or het and $R^7$-$R^{12}$ represent alkyl, aryl or het. Alternatively, $X^2$ represents Ar. Preferably, when $X^2$ represents Ar, the group is substituted by a $C_1$-$C_7$ alkyl group, O—$C_1$-$C_7$ alkyl group, —CN, —F, —Si(alkyl)$_3$, —COOalkyl, —C(O)—, or —$CF_3$. Preferably, the Ar group is substituted at the carbon adjacent the Q bonded ring carbon i.e. the ortho position in a phenyl ring.

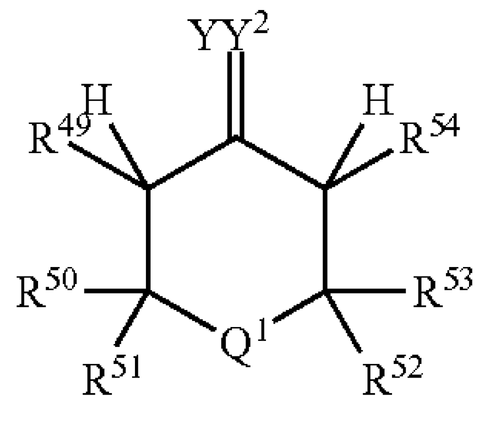
Particularly preferred is when the organic groups $R^7$-$R^9$ and/or $R^{10}$-$R^{12}$ or, alternatively, $R^7$-$R^{12}$ when associated with their respective tertiary carbon atom(s) form composite groups which are at least as sterically hindering as t-butyl(s).

The steric groups may be cyclic, part-cyclic or acyclic. When cyclic or part cyclic, the group may be substituted or unsubstituted or saturated or unsaturated. The cyclic or part cyclic groups may preferably contain, including the tertiary carbon atom(s), from $C_4$-$C_{34}$, more preferably $C_8$-$C_{24}$, most preferably $C_{10}$-$C_{20}$ carbon atoms in the cyclic structure. The cyclic structure may be substituted by one or more substituents selected from halo, cyano, nitro, $OR^{19}$, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $SR^{29}$, $C(O)SR^{30}$, $C(S)NR^{27}R^{28}$, aryl or Het, wherein $R^{19}$ to $R^{30}$ each independently represent hydrogen, aryl or alkyl, and/or be interrupted by one or more oxygen or sulphur atoms, or by silano or dialkylsilicon groups.

In particular, when cyclic, $X^3$ and/or $X^4$ may represent congressyl, norbornyl, 1-norbornadienyl or adamantyl.

$X^3$ and $X^4$ together with $Q^1$ to which they are attached may form an optionally substituted 2-Q1-tricyclo[3.3.1.1{3,7}] decyl group or derivative thereof, or $X^3$ and $X^4$ together with $Q^1$ to which they are attached may form a ring system of formula 1b

(1b)




Alternatively, one or more of the groups $X^3$ and/or $X^4$ may represent a solid phase to which the ligand is attached.



Particularly preferred is when $X^3$ and $X^4$ are the same and $X^1$ and $X^2$ are the same.

In preferred embodiments, $R^4$ to $R^5$ each independently represent hydrogen, alkyl, aryl, or Het and $R^7$ to $R^{12}$ each independently represent alkyl, aryl, or Het;

$R^{19}$ to $R^{30}$ each independently represent hydrogen, alkyl, aryl or Het;

$R^{49}$ and $R^{54}$, when present, each independently represent hydrogen, alkyl or aryl;

$R^{50}$ to $R^{53}$, when present, each independently represent alkyl, aryl or Het;

$YY^2$, when present, independently represents oxygen, sulfur or N—$R^{55}$, wherein $R^{55}$ represents hydrogen, alkyl or aryl.

Preferably, $R^4$ to $R^5$ and $R^7$ to $R^{12}$ when not hydrogen each independently represent alkyl or aryl. More preferably, $R^4$ to $R^5$ and $R^7$ to $R^{12}$ each independently represent $C_1$ to $C_6$ alkyl, $C_1$-$C_6$ alkyl phenyl (wherein the phenyl group is optionally substituted as aryl as defined herein) or phenyl (wherein the phenyl group is optionally substituted as aryl as defined herein). Even more preferably, $R^4$ to $R^5$ and $R^7$ to $R^{12}$ each independently represent $C_1$ to $C_6$ alkyl, which is optionally substituted as alkyl as defined herein. Most preferably, $R^4$ to $R^5$ and $R^7$ to $R^{12}$ each represent non-substituted $C_1$ to $C_8$ alkyl such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, pentyl, hexyl and cyclohexyl, especially methyl.

In a particularly preferred embodiment of the present invention $R^7$ and $R^{10}$ each represent the same alkyl, aryl or Het moiety as defined herein, $R^8$ and $R^{11}$ each represent the same alkyl, aryl or Het moiety as defined herein, and $R^9$ and $R^{12}$ each represent the same alkyl, aryl or Het moiety as defined herein. More preferably $R^7$ and $R^{10}$ each represent the same $C_1$-$C_6$ alkyl, particularly non-substituted $C_1$-$C_6$ alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, pentyl, hexyl or cyclohexyl; $R^8$ and $R^{11}$ each independently represent the same $C_1$-$C_6$ alkyl as defined above; and $R^9$ and $R^{12}$ each independently represent the same $C_1$-$C_6$ alkyl as defined above. For example: $R^7$ and $R^{16}$ each represent methyl; $R^8$ and $R^{11}$ each represent ethyl; and $R^9$ and $R^{12}$ each represent n-butyl or n-pentyl.

In an especially preferred embodiment of the present invention each $R^7$ to $R^{12}$ group represents the same alkyl, aryl, or Het moiety as defined herein. Preferably, when alkyl groups, each $R^7$ to $R^{12}$ represents the same $C_1$ to $C_6$ alkyl group, particularly non-substituted $C_1$-$C_6$ alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, pentyl, hexyl and cyclohexyl. More preferably, each $R^7$ to $R^{12}$ represents methyl or tert-butyl, most preferably, methyl.

The adamantyl, congressyl, norbornyl or 1-norborndienyl group may optionally comprise, besides hydrogen atoms, one or more substituents selected from alkyl, —$OR^{19}$, —$OC(O)R^{20}$, halo, nitro, —$C(O)R^{21}$, —$C(O)OR^{22}$, cyano, aryl, —$N(R^{23})R^{24}$, —$C(O)N(R^{25})R^{26}$, —$C(S)N(R^{27})R^{28}$, —$SR^{29}$, —$C(O)SR^{30}$, —$CF_3$, —$P(R^{56})R^{57}$, —$PO(R^{58})(R^{59})$, —$PO_3H_2$, —$PO(OR^{60})(OR^{61})$, or —$SO_3R^{62}$, wherein $R^{19}$-$R^{30}$, alkyl, halo, cyano and aryl are as defined herein and $R^{56}$ to $R^{62}$ each independently represent hydrogen, alkyl, aryl or Het.

Suitably, when the adamantyl, congressyl, norbornyl or 1-norborndienyl group is substituted with one or more substituents as defined above, highly preferred substituents include unsubstituted $C_1$ to $C_8$ alkyl, —$OR^{19}$, —$OC(O)R^{20}$, phenyl, —$C(O)OR^{22}$, fluoro, —$SO_3H$, —$N(R^{23})R^{24}$, —$P(R^{56})R^{57}$, —$C(O)N(R^{25})R^{26}$ and —$PO(R^{58})(R^{59})$, —$CF_3$, wherein $R^{19}$ represents hydrogen, unsubstituted $C_1$-$C_8$ alkyl or phenyl, $R^{20}$, $R^{22}$, $R^{23}$, $R^{24}$, $R^{25}$, $R^{26}$ each independently represent hydrogen or unsubstituted $C_1$-$C_8$

alkyl, $R^{56}$ to $R^{59}$ each independently represent unsubstituted $C_1$-$C_8$ alkyl or phenyl. In a particularly preferred embodiment the substituents are $C_1$ to $C_8$ alkyl, more preferably, methyl such as found in 1,3 dimethyl adamantyl.

Suitably, the adamantyl, congressyl, norbornyl or 1-norborndienyl group may comprise, besides hydrogen atoms, up to 10, substituents as defined above, preferably up to 5 substituents as defined above, more preferably up to 3 substituents as defined above. Suitably, when the adamantyl, congressyl, norbornyl or 1-norborndienyl group comprises, besides hydrogen atoms, one or more substituents as defined herein, preferably each substituent is identical. Preferred substituents are unsubstituted $C_1$-$C_8$ alkyl and trifluoromethyl, particularly unsubstituted $C_1$-$C_8$ alkyl such as methyl. A highly preferred adamantyl, congressyl, norbornyl or 1-norborndienyl group comprises hydrogen atoms only i.e. the adamantyl congressyl, norbornyl or 1-norborndienyl group is not substituted.

Preferably, when more than one adamantyl, congressyl, norbornyl or 1-norborndienyl group is present in a compound of formula I, each such group is identical.

The 2-$Q^1$-tricyclo[3.3.1.1.{3,7}]decyl group (referred to hereinafter as a 2-meta-adamantyl group for convenience wherein 2-meta-adamantyl is a reference to $Q^1$ being an arsenic, antimony or phosphorus atom i.e. 2-arsa-adamantyl and/or 2-stiba-adamantyl and/or 2-phospha-adamantyl, preferably, 2-phospha-adamantyl) may optionally comprise, beside hydrogen atoms, one or more substituents. Suitable substituents include those substituents as defined herein in respect of the adamantyl group. Highly preferred substituents include alkyl, particularly unsubstituted $C_1$-$C_8$ alkyl, especially methyl, trifluoromethyl, —$OR^{19}$ wherein $R^{19}$ is as defined herein particularly unsubstituted $C_1$-$C_8$ alkyl or aryl, and 4-dodecylphenyl. When the 2-meta-adamantyl group includes more than one substituent, preferably each substituent is identical.

Preferably, the 2-meta-adamantyl group is substituted on one or more of the 1, 3, 5 or 7 positions with a substituent as defined herein. More preferably, the 2-meta-adamantyl group is substituted on each of the 1, 3 and 5 positions. Suitably, such an arrangement means the $Q^1$ atom of the 2-meta-adamantyl group is bonded to carbon atoms in the adamantyl skeleton having no hydrogen atoms. Most preferably, the 2-meta-adamantyl group is substituted on each of the 1, 3, 5 and 7 positions. When the 2-meta-adamantyl group includes more than 1 substituent preferably each substituent is identical. Especially preferred substituents are unsubstituted $C_1$-$C_8$ alkyl and haloalkyls, particularly unsubstituted $C_1$-$C_8$ alkyl such as methyl and fluorinated $C_1$-$C_8$ alkyl such as trifluoromethyl.

Preferably, 2-meta-adamantyl represents unsubstituted 2-meta-adamantyl or 2-meta-adamantyl substituted with one or more unsubstituted $C_1$-$C_8$ alkyl substituents, or a combination thereof.

Preferably, the 2-meta-adamantyl group includes additional heteroatoms, other than the 2-Q atom, in the 2-meta-adamantyl skeleton. Suitable additional heteroatoms include oxygen and sulphur atoms, especially oxygen atoms. More preferably, the 2-meta-adamantyl group includes one or more additional heteroatoms in the 6, 9 and 10 positions. Even more preferably, the 2-meta-adamantyl group includes an additional heteroatom in each of the 6, 9 and 10 positions. Most preferably, when the 2-meta-adamantyl group includes two or more additional heteroatoms in the 2-meta-adamantyl skeleton, each of the additional heteroatoms are identical. Preferably, the 2-meta-adamantyl includes one or more oxygen atoms in the 2-meta-adamantyl skeleton. An especially preferred 2-meta-adamantyl group, which may optionally be substituted with one or more substituents as defined herein, includes an oxygen atom in each of the 6, 9 and 10 positions of the 2-meta-adamantyl skeleton.

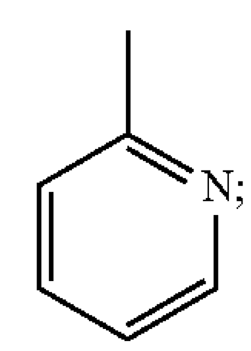
Highly preferred 2-meta-adamantyl groups as defined herein include 2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxadamantyl, 2-phospha-1,3,5-trimethyl-6,9,10-trioxadamantyl, 2-phospha-1,3,5,7-tetra(trifluoromethyl)-6,9,10-trioxadamantyl group, and 2-phospha-1,3,5-tri(trifluoromethyl)-6,9,10-trioxadamantyl group. Most preferably, the 2-phospha-adamantyl is selected from 2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxadamantyl group or 2-phospha-1,3,5, -trimethyl-6,9,10-trioxadamantyl group.

The 2-meta-adamantyl group may be prepared by methods well known to those skilled in the art. Suitably, certain 2-phospha-adamantyl compounds are obtainable from Cytec Canada Inc, Canada. Likewise corresponding 2-meta-adamantyl compounds of formula I etc may be obtained from the same supplier or prepared by analogous methods.

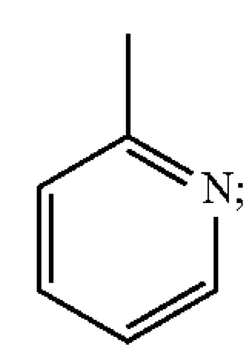
Subject to the restrictions of the claims, preferred embodiments of the present invention include those wherein:

$X^3$ represents $CR^7(R^9)(R^9)$, $X^4$ represents $CR^{19}(R^{11})$ $(R^{12})$, $X^1$ represents $C(R^{101}R^{102})NR^{101}R^{102}$ and $X^2$ represents $C(R^{101}R^{102})NR^{101}R^{102}$;

$X^3$ represents $CR^7(R^8)(R^9)$, $X^4$ represents $CR^{10}(R^{11})(R^{12})$, and $X^1$ and $X^2$ represent



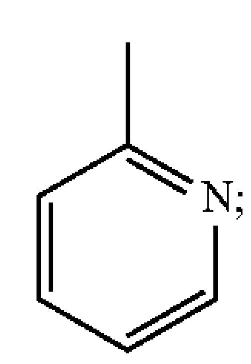
$X^3$ represents $CR^7(R^8)(R^9)$, $X^4$ represents adamantyl, and $X^1$ and $X^2$ represent



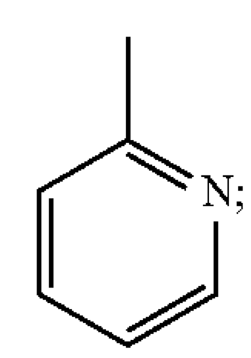
$X^3$ represents $CR^7(R^8)(R^9)$, $X^4$ represents adamantyl and $X^1$ represents $C(R^{101}R^{102})NR^{101}R^{102}$ and $X^2$ represents $C(R^{101}R^{102})NR^{101}R^{102}$;

$X^3$ represents $CR^7(R^8)(R^9)$, $X^4$ represents congressyl, and $X^1$ represents $C(R^{101}R^{102})NR^{101}R^{102}$ and $X^2$ represents $C(R^{101}R^{102})NR^{101}R^{102}$;

$X^3$ represents $CR^7(R^8)(R^9)$, $X^4$ represents congressyl, and $X^1$ and $X^2$ represent



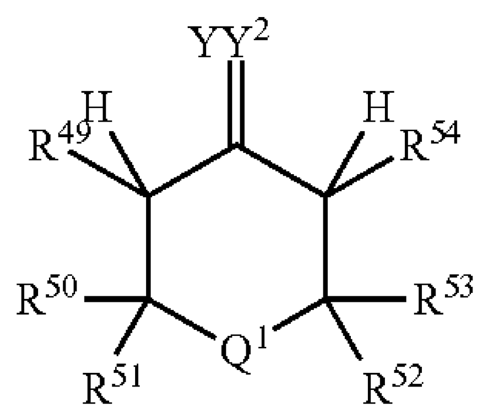
$X^3$ and $X^4$ independently represent adamantyl, and $X^1$ and $X^2$ represent



$X^3$ and $X^4$ independently represent adamantyl, and $X^1$ represents $C(R^{101}R^{102})NR^{101}R^{102}$ and $X^2$ represents $C(R^{101}R^{102})NR^{101}R^{102}$;

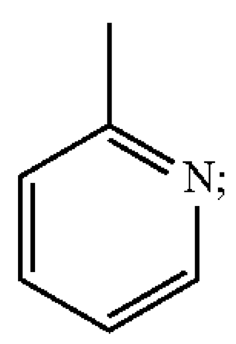
$X^3$ and $X^4$ together with $Q^1$ to which they are attached may form a ring system of formula 1b

(1b)



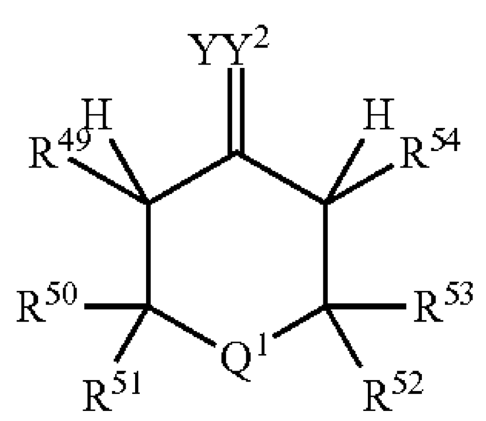
and $X^1$ represents $C(R^{101}R^{102})NR^{101}R^{102}$ and $X^2$ represents $C(R^{101}R^{102})NR^{101}R^{102}$;

$X^3$ and $X^4$ independently represent congressyl, and $X^1$ and $X^2$ represent

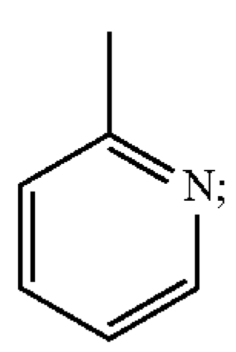


$X^3$ and $X^4$ together with $Q^1$ to which they are attached may form a ring system of formula 1b

(1b)



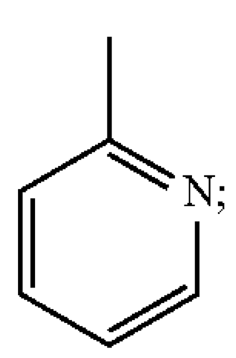
and $X^1$ and $X^2$ represent



$X^3$ and $X^4$ independently represent congressyl, and $X^1$ represents $C(R^{101}R^{102})NR^{101}R^{102}$ and $X^2$ represents $C(R^{101}R^{102})NR^{101}R^{102}$;

$X^3$ and $X^4$ together with $Q^1$ to which they are attached form a 2-phospha-adamantyl group, and $X^1$ represents $C(R^{101}R^{102})NR^{101}R^{102}$ and $X^2$ represents $C(R^{101}R^{102})NR^{101}R^{102}$;

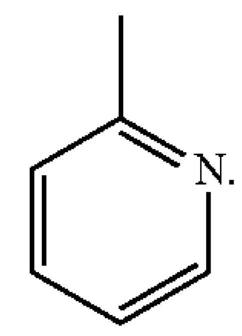
$X^3$ and $X^4$ together with $Q^1$ to which they are attached form a 2-phospha-adamantyl group, and $X^1$ and $X^2$ represent



Highly preferred embodiments of the present invention include those wherein:

$X^3$ represents $CH^7(R^8)(R^9)$, $X^4$ represents $CR^{10}(R^{11})(R^{12})$, $X^1$ represents $C(R^{101}R^{102})NR^{101}R^{102}$ and $X^2$ represents $C(R^{101}R^{102})NR^{101}R^{102}$; especially where $R^7$-$R^{12}$ are methyl and $R^{101}$ and $R^{102}$ are either hydrogen, methyl or ethyl; and

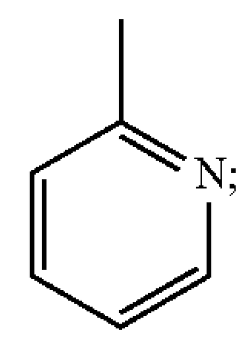
$X^3$ represents $CR^7(R^8)(R^9)$, $X^4$ represents $CR^{10}(R^{11})(R^{12})$, and $X^1$ and $X^2$ represent



Preferably in a compound of formula I, $X^3$ is identical to $X^4$ and/or $X^1$ is identical to $X^2$.

Particularly preferred combinations in the present invention include those wherein: —

(1) represents $CR^7(R^8)(R^9)$, $X^4$ represents $CR^{10}(R^{11})(R^{12})$ and $X^1$ and $X^2$ represent



A and B are the same and represent —$CH_2$—;

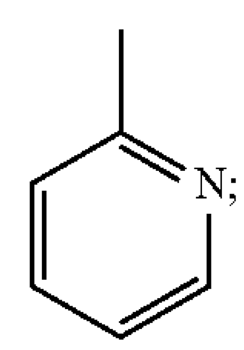
$Q^1$ and $Q^2$ both represent phosphorus linked to the R group at ring positions 1 and 2.

(2) $X^3$ represents $CR^7(R^8)(R^9)$, $X^4$ represents $CR^{10}(R^{11})(R^{12})$, $X^1$ represents $C(R^{101}R^{102})NR^{101}R^{102}$ and $X^2$ represents $C(R^{101}R^{102})NR^{101}R^{102}$;

A and B are the same and represent —$CH_2$—;

$Q^1$ and $Q^2$ both represent phosphorus linked to the R group at ring positions 1 and 2.

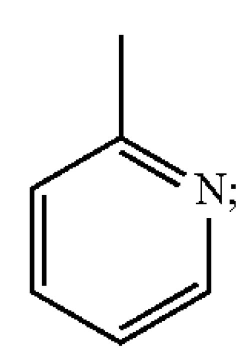
(3) $X^3$ and $X^4$ together with $Q^1$ to which they are attached form a 2-phospha-adamantyl group, and $X^1$ and $X^2$ represent



A and B are the same and represent —$CH_2$—;

$Q^1$ and $Q^2$ both represent phosphorus linked to the R group at ring positions 1 and 2.

(4) $X^3$ and $X^4$ represent adamantyl and $X^1$ and $X^2$ represent



A and B are the same and represent —$CH_2$—;

$Q^1$ and $Q^2$ both represent phosphorus linked to the R group at ring positions 1 and 2.

Preferably, in the above embodiments, $R^{101}$ and $R^{102}$ are hydrogen, methyl or ethyl.

Preferably, in the compound of formula I, A and B each independently represents $C_1$ to $C_6$ alkylene which is optionally substituted as defined herein, for example with alkyl groups. Preferably, the lower alkylene groups which A and B represent are non-substituted. Particularly preferred alkylenes which A and B may independently represent are —$CH_2$— or —$C_2H_4$—. Most preferably, each of A and B represent the same alkylene as defined herein, particularly —$CH_2$—. Alternatively, one of A or B is omitted ie $Q^2$ or $Q^1$ is connected directly to the group R and the other Q group is not connected directly to the group R and is a $C_1$ to $C_6$ alkylene, preferably —$CH_2$— or —$C_2H_4$—, most preferably, —$CH_2$—.

Still further preferred compounds of formula I include those wherein:

$R^7$ to $R^{12}$ are alkyl and are the same and preferably, each represents $C_1$ to $C_6$ alkyl, particularly methyl.

Especially preferred specific compounds of formula I include those wherein:

each $R^7$ to $R^{12}$ is the same and represents methyl;

A and B are the same and represent —$CH_2$—;

R represents benzene-1,2-diyl.

The invention not only extends to novel bidentate ligands of formula (I) but also novel complexes of such ligands with the metal of Group 8, 9 or 10 or a compound thereof.

## DEFINITIONS

The term "lower alkylene" which A and B represent in a compound of formula I, when used herein, includes $C_0$-$C_{10}$ or $C_1$ to $C_{10}$ groups, preferably, $C_0$, $C_1$ or $C_2$, more preferably, $C_1$, most preferably, methylene which, in the case of $C_1$ to $C_{10}$, can be bonded at two places on the group to thereby connect the group $Q^1$ or $Q^2$ to the R group, and, in the latter case, is otherwise defined in the same way as "alkyl" below. Nevertheless, in the latter case, methylene is most preferred. In the former case, by $C_0$ is meant that the group $Q^1$ or $Q^2$ is connected directly to the R group and there is no $C_1$-$C_{10}$ lower alkylene group and in this case only one of A and B is a $C_1$-$C_{10}$ lower alkylene. In any case, when one of the groups A or B is $C_0$ then the other group cannot be $C_0$ and must be a $C_1$-$C_{10}$ group as defined herein and, therefore, at least one of A and B is a $C_1$-$C_{10}$ "lower alkylene" group.

The term "alkyl" when used herein, means $C_1$ to $C_{10}$ alkyl, preferably, $C_1$ to $C_6$ alkyl, more preferably, $C_1$ to $C_4$ alkyl and includes methyl, ethyl, ethenyl, propyl, propenyl butyl, butenyl, pentyl, pentenyl, hexyl, hexenyl and heptyl groups. Unless otherwise specified, alkyl groups may, when there is a sufficient number of carbon atoms, be linear or branched (particularly preferred branched groups include t-butyl and isopropyl), be saturated or unsaturated, be cyclic, acyclic or part cyclic/acyclic, be unsubstituted, substituted or terminated by one or more substituents selected from halo, cyano, nitro, $OR^{19}$, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $SR^{29}$, $C(O)SR^{30}$, $C(S)NR^{27}R^{28}$, unsubstituted or substituted aryl, or unsubstituted or substituted Het and/or be interrupted by one or more (preferably less than 4) oxygen, sulphur, silicon atoms, or by silano or dialkylsilicon groups, or mixtures thereof.

The term "fluoroalkyl" is defined in the same way as alkyl except any one or more of the hydrogen groups may be replaced by a fluoride.

$R^4$, $R^5$, $R^7$ to $R^{12}$ and $R^{13}$-$R^{18}$ each independently represent alkyl, aryl, or Het unless $X^2$ is joined to the $Q^2$ atom via a non tertiary carbon in which case they can each also represent hydrogen.

$R^{19}$ to $R^{30}$ herein each independently represent hydrogen, halo, unsubstituted or substituted aryl or unsubstituted or substituted alkyl, or, in the case of $R^{21}$, additionally, halo, nitro, cyano, thio and amino. Preferably, $R^{19}$ to $R^{30}$ represents hydrogen, unsubstituted $C_1$-$C_8$ alkyl or phenyl, more preferably, hydrogen or unsubstituted $C_1$-$C_8$ alkyl.

$R^{49}$ and $R^{54}$ each independently represent hydrogen, alkyl or aryl. $R^{50}$ to $R^{53}$ each independently represent alkyl, aryl or Het. $YY^1$ and $YY^2$ each independently represent oxygen, sulfur or N—$R^{55}$, wherein $R^{55}$ represents hydrogen, alkyl or aryl.

$R^{101}$ and $R^{102}$ represent optional substituents hydrogen, aryl, alkyl or fluoroalkyl

The term "Ar" or "aryl" when used herein, includes five-to-ten-membered, preferably five to eight membered, carbocyclic aromatic or pseudo aromatic groups, such as phenyl, cyclopentadienyl and indenyl anions and naphthyl, which groups may be unsubstituted or as one option substituted with one or more substituents selected from unsubstituted or substituted aryl, alkyl (which group may itself be unsubstituted or substituted or terminated as defined herein), Het (which group may itself be unsubstituted or substituted or terminated as defined herein), halo, cyano, nitro, $OR^{19}$, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $SR^{29}$, $C(O)SR^{30}$ or $C(S)NR^{27}R^{28}$ wherein $R^{19}$ to $R^{30}$ are as defined herein.

The term "alkenyl" when used herein, means $C_2$ to alkenyl, preferably, $C_1$ to $C_6$ alkenyl, more preferably, $C_1$ to $C_4$ alkenyl and includes ethenyl, propenyl, butenyl, pentenyl, and hexenyl groups. Unless otherwise specified, alkenyl groups may, when there is a sufficient number of carbon atoms, be linear or branched, be saturated or unsaturated, be cyclic, acyclic or part cyclic/acyclic, be unsubstituted, substituted or terminated by one or more substituents selected from halo, cyano, nitro, $OR^{19}$, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $SR^{29}$, $C(O)SR^{30}$, $C(S)NR^{27}R^{28}$, unsubstituted or substituted aryl, or unsubstituted or substituted Het, wherein $R^{19}$ to $R^{30}$ are defined herein and/or be interrupted by one or more (preferably less than 4) oxygen, sulphur, silicon atoms, or by silano or dialkylsilicon groups, or mixtures thereof.

The term "alkynyl" when used herein, means $C_2$ to $C_{10}$ alkynyl, preferably, $C_1$ to $C_6$ alkynyl, more preferably, $C_1$ to $C_4$ alkynyl and includes ethynyl, propynyl, butynyl, pentynyl, and hexynyl groups. Unless otherwise specified, alkynyl groups may, when there is a sufficient number of carbon atoms, be linear or branched, be saturated or unsaturated, be cyclic, acyclic or part cyclic/acyclic, be unsubstituted, substituted or terminated by one or more substituents selected from halo, cyano, nitro, $OR^{19}$, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $SR^{29}$, $C(O)SR^{30}$, $C(S)NR^{27}R^{28}$, unsubstituted or substituted aryl, or unsubstituted or substituted Het, wherein $R^{19}$ to $R^{30}$ are defined herein and/or be interrupted by one or more (preferably less than 4) oxygen, sulphur, silicon atoms, or by silano or dialkylsilicon groups, or mixtures thereof.

The terms "aralkyl", "alkaryl", "arylenealkyl" or the like should, in the absence of information to the contrary, be taken to be in accordance with the above definition of "alkyl" as far as the alkyl or alk portion of the group is concerned.

The above Ar or aryl groups may be attached by one or more covalent bonds but references to "arylene" or "arylenealkyl" or the like herein should be understood as two covalent bond attachment but otherwise be defined as Ar or aryl above as far as the arylene portion of the group is concerned. References to "alkaryl", "aralkyl" or the like should be taken as references to Ar or aryl above as far as the Ar or aryl portion of the group is concerned.

Halo groups with which the above-mentioned groups may be substituted or terminated include fluoro, chloro, bromo and iodo.

The term "Het", when used herein, includes four- to twelve-membered, preferably four- to ten-membered ring systems, which rings contain one or more heteroatoms selected from nitrogen, oxygen, sulfur and mixtures thereof, and which rings contain no, one or more double bonds or may be non-aromatic, partly aromatic or wholly aromatic in character. The ring systems may be monocyclic, bicyclic or fused. Each "Het" group identified herein may be unsubstituted or substituted by one or more substituents selected from halo, cyano, nitro, oxo, alkyl (which alkyl group may itself be unsubstituted or substituted or terminated as defined herein) —$OR^{19}$, —$OC(O)R^{23}$, —$C(O)R^{21}$, —$C(O)OR^{22}$, —$N(R^{23})R^{24}$, —$C(O)N(R^{25})R^{26}$, —$SR^{29}$, —$C(O)SR^{30}$ or —$C(S)N(R^{27})R^{28}$ wherein $R^{19}$ to $R^{30}$ are as defined herein The term "Het" thus includes groups such as optionally substituted azetidinyl, pyrrolidinyl, imidazolyl, indolyl, furanyl, oxazolyl, isoxazolyl, oxadiazolyl, thiazolyl, thiadiazolyl, triazolyl, oxatriazolyl, thiatriazolyl, pyridazinyl, morpholinyl, pyrimidinyl, pyrazinyl, quinolinyl, isoquinolinyl, piperidinyl, pyrazolyl and piperazinyl. Substitution at Het may be at a carbon atom of the Het ring or, where appropriate, at one or more of the heteroatoms.

"Het" groups may also be in the form of an N oxide.

The term hetero as mentioned herein means nitrogen, oxygen, sulfur or mixtures thereof.

The catalyst compounds of the present invention may act as a "heterogeneous" catalyst or a "homogeneous" catalyst, preferably, a homogenous catalyst.

By the term "homogeneous" catalyst we mean a catalyst, i.e. a compound of the invention, which is not supported but is simply admixed or formed in-situ with the reactants of the carbonylation reaction, preferably in a suitable solvent as described herein.

By the term "heterogeneous" catalyst we mean a catalyst, i.e. the compound of the invention, which is carried on a support.

Where a compound of a formula herein (e.g. formula I) contains an alkenyl group or a cycloalkyl moiety as defined, cis (E) and trans (Z) isomerism may also occur. The present invention includes the individual stereoisomers of the compounds of any of the formulas defined herein and, where appropriate, the individual tautomeric forms thereof, together with mixtures thereof. Separation of diastereoisomers or cis and trans isomers may be achieved by conventional techniques, e.g. by fractional crystallisation, chromatography or H.P.L.C. of a stereoisomeric mixture of a compound one of the formulas or a suitable salt or derivative thereof. An individual enantiomer of a compound of one of the formulas may also be prepared from a corresponding optically pure intermediate or by resolution, such as by H.P.L.C. of the corresponding racemate using a suitable chiral support or by fractional crystallisation of the diastereoisomeric salts formed by reaction of the corresponding racemate with a suitable optically active acid or base, as appropriate.

Support and Dispersant

According to a further aspect, the present invention provides a process for the carbonylation of an ethylenically unsaturated compound as defined herein wherein the process is carried out with the catalyst comprising a support, preferably an insoluble support.

Preferably, the support comprises a polymer such as a polyolefin, polystyrene or polystyrene copolymer such as a divinylbenzene copolymer or other suitable polymers or copolymers known to those skilled in the art; a silicon derivative such as a functionalised silica, a silicone or a silicone rubber; or other porous particulate material such as for example inorganic oxides and inorganic chlorides.

Preferably the support material is porous silica which has a surface area in the range of from 10 to 700 $m^2/g$, a total pore volume in the range of from 0.1 to 4.0 cc/g and an average particle size in the range of from 10 to 500 μm. More preferably, the surface area is in the range of from 50 to 500 $m^2/g$, the pore volume is in the range of from 0.5 to 2.5 cc/g and the average particle size is in the range of from 20 to 200 μm. Most desirably the surface area is in the range of from 100 to 400 $m^2/g$, the pore volume is in the range of from 0.8 to 3.0 cc/g and the average particle size is in the range of from 30 to 100 μm. The average pore size of typical porous support materials is in the range of from 10 to 1000 Å. Preferably, a support material is used that has an average pore diameter of from 50 to 500 Å, and most desirably from 75 to 350 Å. It may be particularly desirable to dehydrate the silica at a temperature of from 100° C. to 800° C. anywhere from 3 to 24 hours.

Suitably, the support may be flexible or a rigid support, the insoluble support is coated and/or impregnated with the compounds of the process of the invention by techniques well known to those skilled in the art.

Alternatively, the compounds of the process of the invention are fixed to the surface of an insoluble support, optionally via a covalent bond, and the arrangement optionally includes a bifunctional spacer molecule to space the compound from the insoluble support.

The compounds of the invention may be fixed to the surface of the insoluble support by promoting reaction of a functional group present in the compound of formula I with a complimentary reactive group present on or previously inserted into the support. The combination of the reactive group of the support with a complimentary substituent of the compound of the invention provides a heterogeneous catalyst where the compound of the invention and the support are linked via a linkage such as an ether, ester, amide, amine, urea, keto group.

The choice of reaction conditions to link a compound of the process of the present invention to the support depends upon the groups of the support. For example, reagents such as carbodiimides, 1,1'-carbonyldiimidazole, and processes such as the use of mixed anhydrides, reductive amination may be employed.

According to a further aspect, the present invention provides the use of the process or catalyst of any aspect of the invention wherein the catalyst is attached to a support.

Additionally, the bidentate ligand may be bonded to a suitable polymeric substrate via at least one of the bridge substituents (including cyclic atoms), the bridging group X, the linking group A or the linking group B e.g. 1-(di-t-butylphosphinomethyl)-2-(di-pyridin-2-ylphosphinomethyl) benzene may be bonded, preferably, via the 3, 4, 5 or 6 cyclic carbons of the benzene group to polystyrene to give an immobile heterogeneous catalyst.

The use of stabilising compounds with the catalyst system may also be beneficial in improving recovery of metal which has been lost from the catalyst system. When the catalyst system is utilized in a liquid reaction medium such stabilizing compounds may assist recovery of the group 8, 9 or 10 metal.

Preferably, therefore, the catalyst system includes in a liquid reaction medium a polymeric dispersant dissolved in a liquid carrier, said polymeric dispersant being capable of stabilising a colloidal suspension of particles of the group 8, 9 or 10 metal or metal compound of the catalyst system within the liquid carrier.

The liquid reaction medium may be a solvent for the reaction or may comprise one or more of the reactants or reaction products themselves. The reactants and reaction products in liquid form may be miscible with or dissolved in a solvent or liquid diluent.

The polymeric dispersant is soluble in the liquid reaction medium, but should not significantly increase the viscosity of the reaction medium in a way which would be detrimental to reaction kinetics or heat transfer. The solubility of the dispersant in the liquid medium under the reaction conditions of temperature and pressure should not be so great as to deter significantly the adsorption of the dispersant molecules onto the metal particles.

The polymeric dispersant is capable of stabilising a colloidal suspension of particles of said group 8, 9 or 10 metal or metal compound within the liquid reaction medium such that the metal particles formed as a result of catalyst degradation are held in suspension in the liquid reaction medium and are discharged from the reactor along with the liquid for reclamation and optionally for re-use in making further quantities of catalyst. The metal particles are normally of colloidal dimensions, e.g. in the range 5-100 nm average particle size although larger particles may form in some cases. Portions of the polymeric dispersant are adsorbed onto the surface of the metal particles whilst the remainder of the dispersant molecules remain at least partially solvated by the liquid reaction medium and in this way the dispersed group 8, 9 or 10 metal particles are stabilised against settling on the walls of the reactor or in reactor dead spaces and against forming agglomerates of metal particles which may grow by collision of particles and eventually coagulate. Some agglomeration of particles may occur even in the presence of a suitable dispersant but when the dispersant type and concentration is optimised then such agglomeration should be at a relatively low level and the agglomerates may form only loosely so that they may be broken up and the particles redispersed by agitation.

The polymeric dispersant may include homopolymers or copolymers including polymers such as graft copolymers and star polymers.

Preferably, the polymeric dispersant has sufficiently acidic or basic functionality to substantially stabilise the colloidal suspension of said group 8, 9 or 10 metal or metal compound.

By substantially stabilise is meant that the precipitation of the group 8, 9 or 10 metal from the solution phase is substantially avoided.

Particularly preferred dispersants for this purpose include acidic or basic polymers including carboxylic acids, sulphonic acids, amines and amides such as polyacrylates or heterocycle, particularly nitrogen heterocycle, substituted polyvinyl polymers such as polyvinyl pyrrolidone or copolymers of the aforesaid.

Examples of such polymeric dispersants may be selected from polyvinylpyrrolidone, polyacrylamide, polyacrylonitrile, polyethylenimine, polyglycine, polyacrylic acid, polymethacrylic acid, poly(3-hydroxybutyricacid), poly-L-leucine, poly-L-methionine, poly-L-proline, poly-L-serine, poly-L-tyrosine, poly(vinylbenzenesulphonic acid) and poly (vinylsulphonic acid), acylated polyethylenimine. Suitable acylated polyethylenimines are described in BASF patent publication EP1330309 A1 and U.S. Pat. No. 6,723,882.

Preferably, the polymeric dispersant incorporates acidic or basic moieties either pendant or within the polymer backbone. Preferably, the acidic moieties have a dissociation constant ($pK_a$) of less than 6.0, more preferably, less than 5.0, most preferably less than 4.5. Preferably, the basic moieties have a base dissociation constant ($pK_b$) being of less than 6.0, more preferably less than 5.0 and most preferably less than 4.5, $pK_a$ and $pK_b$ being measured in dilute aqueous solution at 18° C.

Suitable polymeric dispersants, in addition to being soluble in the reaction medium at reaction conditions, contain at least one acidic or basic moiety, either within the polymer backbone or as a pendant group. We have found that polymers incorporating acid and amide moieties such as polyvinylpyrrolidone (PVP) and polyacrylates such as polyacrylic acid (PAA) are particularly suitable. The molecular weight of the polymer which is suitable for use in the invention depends upon the nature of the reaction medium and the solubility of the polymer therein. We have found that normally the average molecular weight is less than 100,000. Preferably, the average molecular weight is in the range 1,000-200,000, more preferably, 5,000-100,000, most preferably, 10,000-40,000 e.g. Mw is preferably in the range 10,000-80,000, more preferably 20,000-60,000 when PVP is used and of the order of 1,000-10,000 in the case of PAA.

The effective concentration of the dispersant within the reaction medium should be determined for each reaction/catalyst system which is to be used.

The dispersed group 8, 9 or 10 metal may be recovered from the liquid stream removed from the reactor e.g. by filtration and then either disposed of or processed for re-use as a catalyst or other applications. In a continuous process the liquid stream may be circulated through an external heat-exchanger and in such cases it may be convenient to locate filters for the palladium particles in these circulation apparatus.

Preferably, the polymer:metal mass ratio in g/g is between 1:1 and 1000:1, more preferably, between 1:1 and 400:1, most preferably, between 1:1 and 200:1. Preferably, the polymer:metal mass ratio in g/g is up to 1000, more preferably, up to 400, most preferably, up to 200.

Preferably, the carbonylation reaction is an anaerobic reaction. In other words, typically the reaction takes place generally in the absence of oxygen.

Conveniently, the process of the invention may utilise highly stable compounds under typical carbonylation reaction conditions such that they require little or no replenishment. Conveniently, the process of the invention may have a high rate for the carbonylation reaction. Conveniently, the process of the invention may promote high conversion rates, thereby yielding the desired product in high yield with little or no impurities. Consequently, the commercial viability of the carbonylation reaction may be increased by employing the process of the invention. It is especially advantageous that the process of the invention provides a carbonylation reaction with a high TON number.

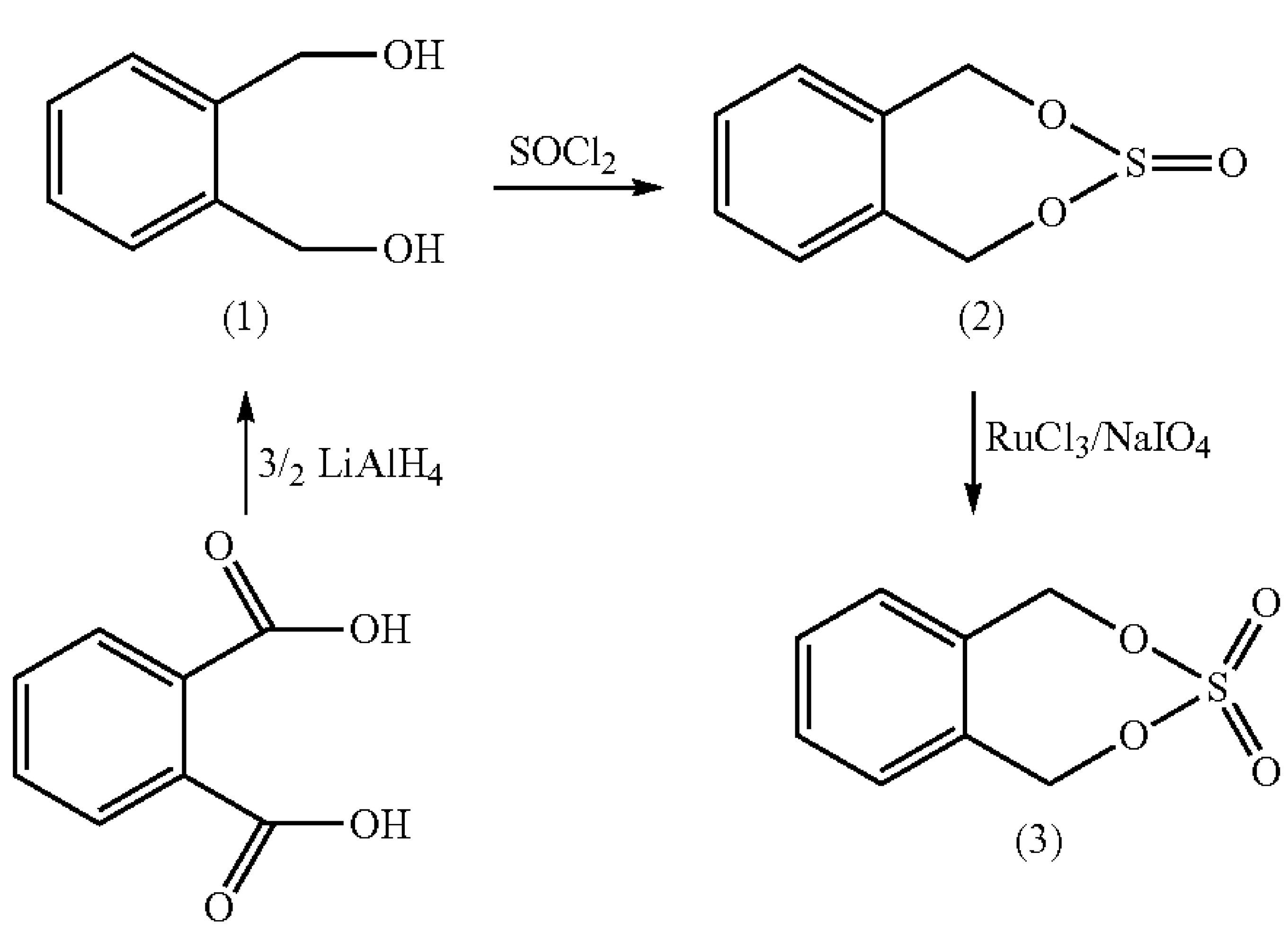
It will be appreciated that any of the features set forth in the first aspect of the invention may be regarded as preferred features of the further aspects of the present invention and vice versa.

The invention will now be described and illustrated by way of the following non-limiting examples and comparative examples

## PREPARATIVE EXAMPLES

### Preparation of Cyclic Sulphate of 1,2-Benzenedimethanol (3)

The method employed for the synthesis of phosphine ligands of the derivatives of the examples starts with the synthesis of the cyclic sulphate (3). The cyclic sulphate compound is formed in a two step synthesis. The commercially available di-alcohol 1,2-benzenedimethanol (1) (which can also be prepared by the lithium aluminium hydride reduction of phthalic acid) was reacted with thionyl chloride ($SOCl_2$) in dichloromethane to give the cyclic sulphite complex (2). The cyclic sulphite complex was then oxidised with sodium periodate and ruthenium trichloride to give the cyclic sulphate complex (3).




Experimental

General

Unless stated to the contrary all manipulations were performed under an atmosphere of Nitrogen using standard Schlenk line, cannula and glovebox techniques. All NMR experiments were performed using $CDCl_3$ as the solvent.

Preparation of Cyclic Sulphate (3)

The dialcohol (1) (21.2 g, 153 mmol) was partially dissolved in dichloromethane (250 ml). To this was added thionyl chloride (13.8 ml, 189 mmol) slowly. This gave a large volume of gas evolution. The resultant solution was then heated to reflux (50° C.) for 90 minutes. The resultant solution was then cooled to room temperature and stirred overnight. At this point the cyclic sulfite complex (2) had been formed. The solvent was then removed under vacuum to give a pale brown oil. The cyclic sulfite was then diluted with dichloromethane (100 ml), acetonitrile (100 ml) and water (150 ml). To the resultant biphasic solution was added sodium periodate (65.3 g, 306 mmol) and Ruthenium trichloride hydrate (300 mg). The resultant suspension was then stirred at room temperature for one hour during this time a large volume of white precipitate was formed. The final suspension was diluted with water (100 ml) and ether (100 ml) added. The organic layer was collected by separation and the aqueous residues washed with ether (2*100 ml). The combined organic extracts were then washed with water (2*200 ml) before being dried over sodium sulphate. The organic extracts were then filtered through filter paper containing celite. This gave an off-colourless solution. The solvent was then removed under vacuum to give an off white solid. The solid was stored in the freezer at −20° C. Yield=24.6 g, 80%. $^1$H NMR (500 MHz, $CDCl_3$, δ), 7.46 (m, 2H, Ph), 7.38 (m, 2H, Ph), 5.44 (s, 4H, $CH_2$) ppm.

Synthesis of 1-(di-tert-butyl)phosphinomethyl)-2-((di-pyridin-2-yl)phosphinomethyl)benzene

Preparation of Tris(pyridin-2-yl)phosphine

2-Bromopyridine (100 g, 633 mmol) was added dropwise over 30 min to a stirred solution of $Bu^nLi$ (2.5M in hexane, 253 ml, 633 mmol) in $Et_2O$ (300 ml) at −78° C. in a 1 L flask. This mixture was stirred at −78° C. for 1 h, then $PCl_3$ (18.4 ml, 211 mmol) added dropwise over 30 min with stirring. The resultant mixture was then stirred for 30 minutes at −78° C. before being allowed to warm up to room temperature and then stirred at room temperature for one hour. The resultant tan mixture was then dried under vacuum and water (300 ml, degassed with nitrogen gas for 30 minutes) added. Chloroform (400 ml) was then added. The biphasic mixture was then stirred for 30 minutes and then the lower (organic phase) was cannula transferred into a clean Schlenk flask. The solvent was then removed under vacuum to give a sticky brown/red solid. To this was added pentane (50 ml) and the pentane stirred into the mixture, this gave a brown/orange solid. The pentane soluble material was removed by cannula and the pentane washing repeated. Again the pentane soluble material was removed by cannula. The residue was then dried under vacuum before being suspended in ethanol (20 ml). The ethanol suspension was then heated up to 80° C. which gave a dark red solution. This was then allowed to cool to room temperature and orange/yellow crystals started to form. The solution was then placed in the freezer at −20° C. overnight. This gave a large amount of red/orange solid. The ethanol soluble material was then removed by cannula and the solid dried under vacuum. This gave a sticky orange solid. Yield=22.4 g, 40%. $^{31}P\{^1H\}$NMR (121 MHz, CDCl3) ä: −0.42 (s, $PPy_2$).

Preparation of Bis(pyridin-2-yl)phosphine ($Py_2PH$)

The tris(pyridin-2-yl)phosphine (22.4 g, 85 mmol) was suspended in THF (400 ml). To this were added lithium granules (5.0 g, 720 mmol). The mixture was then stirred at room temperature for four hours. This gave an intense red solution. The solution was then filtered into a clean Schlenk flask to remove any un-reacted lithium metal. The solvent was then removed under vacuum and water (100 ml, degassed with nitrogen gas for 20 minutes) added. Ether (400 ml) was then added and the biphasic solution stirred for 20 minutes. The upper (organic) phase was then cannula transferred into a clean Schlenk flask and then dried under vacuum. This gave dark orange/red oil. Yield=15.1 g, 94% $^{31}P\{^1H\}$NMR (121 MHz, CDCl3) ä; −33.8 (s, $PPy_2$).

Preparation of di-tert-butylphosphine borane

Di-tert-butylphosphine chloride (34 g, 188.41 mmol) was added to a Schlenk flask followed by diethyl ether (200 ml). The ether solution was cooled in a cold water bath and $LiAlH_4$ (1M in diethyl ether, 100 ml, 100 mmol) was added slowly. This gave a yellow suspension which was stirred at room temperature overnight. The suspension was quenched by the addition of water (50 ml, degassed with nitrogen for 20 minutes). This gave a biphasic solution. The upper (organic layer) was cannula transferred into a clean Schlenk and the aqueous residues washed with a further 100 ml of ether. The ether extracts were combined and dried with sodium sulphate. The ether extracts were then cannula transferred into a clean Schlenk and the ether removed by distillation. This gave a colourless oil. The colourless oil was then diluted with THF (200 ml) and cooled to 0° C., to this was added $BH_3$ in THF

(1M solution, 250 ml, 250 mmol). The resultant solution was then stirred at room temperature overnight. The solvent was then removed under vacuum to give a white crystalline solid which was then isolated in the glovebox. Yield=22.1 g, 73% yield. $^{31}P\ \{^{1}H\}$NMR (80 MHz, $CDCl_3$, δ): δ 49.23 ppm (multiplet).

Synthesis of 1-(di-tert-butylphosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)benzene

A 2.5M solution of $Bu^nLi$ (83 mL, 207.5 mmol) in hexanes was added to a solution of $^tBu_2PH.BH_3$ (33.2 g, 207.5 mmol) in THF (250 mL) at 0°. The mixture was allowed to reach room temperature then stirred for 30 min. After cooling to −78° C., it was added dropwise over 10 min to a pre-cooled (−78° C.) solution of the cyclic sulfate (1,2-$C_6H_4(CH_2O)_2SO_2$) (41.5 g, 207.5 mmol) in THF (300 mL). The mixture was stirred for 30 min at −78° C. and then stirred for 30 min at room temperature. After cooling the mixture to −78° C., it was treated with a solution of $Py_2PLi$ {prepared from $Py_2PH$ (39 g, 207.5 mmol) in THF (250 mL) and $Bu^nLi$ (83 ml of a 2.5M solution in hexane, 207.5 mmol) at −78° C.}. The mixture was allowed to warm to room temperature and then stirred overnight. The solvent was removed under reduced pressure and the residue was re-dissolved in $Et_2O$ (500 mL). The solution was then quenched with water (200 mL). The biphasic mixture was then stirred at room temperature for 30 minutes before the organic (upper) phase was cannula transferred into a clean Schlenk flask. The solvent was then removed under vacuum to give a brown sticky solid. The solid was dissolved in TBME (600 ml) and tetrafluoroboric acid diethyl ether complex (1245 mmol, 171 ml) was then added. This gave the immediate formation of an orange precipitate. The mixture was then heated to reflux for 16 hours. The solvent was then removed under vacuum and the residue treated with a solution of potassium hydroxide (80 g, 1426 mmol) in water (300 ml, degassed with nitrogen gas for 30 minutes). Pentane (500 ml) was then added and the biphasic mixture rapidly stirred for thirty minutes. The upper phase (organic) was then cannula transferred into a clean Schlenk and the solvent removed under vacuum. This gave a sticky viscous red/orange oil, yield 29.4 g, 32% $^{31}P\{^{1}H\}$NMR (121 MHz, $CDCl_3$) ä: −6.5 (s, PPy); 28.5 (s, $PBu^t$)

Synthesis of Pyridylphenylphosphine

A solution of $Cl_2PPh$ (30 mL, 220 mmol) in $Et_2O$ (800 mL) in a 1 L Schlenk flask was cooled to −78° C. and a solution of $HNEt_2$ (46 mL, 440 mmol) added through a dropping funnel over 30 min with stirring. The solution was allowed to rise to room temperature and stood overnight. The resulting yellow solution was cannula transferred into a clean Schlenk flask and the solvent removed under vacuum. To the solid residue was added ether (500 ml) and the mixture rapidly stirred for 1 hour and then stood overnight. The ether extracts were then combined and the dried under vacuum. This gave pale oil. The yellow oil was then dissolved in ether (500 ml) and a solution of LiPy {prepared by adding BrPy (21 mL, 220 mmol) to a solution of BuLi (88 mL of a 2.5 M solution in hexane) in $Et_2O$ (100 mL) dropwise over 30 min at −78° C., the solution was then stirred for 1 h} was added via a cannula over 30 min. The solution was allowed to reach room temperature and was then stirred overnight. This gave a pale brown suspension. HCl (110 mL of a 2 M solution in $Et_2O$) was added over 20 mins with vigorous stirring, generating a large quantity of pale brown precipitate. Further HCl (110 mL of a 2 M solution in $Et_2O$) was added. The suspension was then allowed to stand and the yellow solution cannula transferred into a clean Schlenk flask. The brown precipitate was washed again with THF (500 mL) and the washings combined before removing the THF under vacuum leaving a red/orange solid. The solid was then dissolved in THF (300 mL) then added to an ice cooled solution of magnesium powder (9 g) in THF (100 mL) over 30 mins with stirring. The solution was kept under ice cooling for a further 30 min, then allowed to rise to room temperature and stirring overnight. The solution was filtered to remove excess magnesium and quenched with water (100 mL, degassed with nitrogen gas for 20 minutes). The organic layer was then cannula transferred into a clean Schlenk flask and then dried under vacuum to give viscous orange oil, yield=15.1 g, 36%. $^{31}P$ NMR (121 MHz, $CDCl_3$) ä: −37.79 (d, $J_{PH}$=222 Hz).

Synthesis of 1-(di-tert-butylphosphinomethyl)-2-pyridin-2-ylphenylphosphinomethyl)benzene

A 2.5M solution of $Bu^nLi$ (32.1 mL, 80.2 mmol) in hexanes was added to a solution of $^tBu_2PH.BH_3$ (12.8 g, 80.2 mmol) in THF (150 mL) at 0°. The mixture was allowed to reach room temperature then stirred for 30 min. After cooling to −78° C., it was added dropwise over 10 min to a pre-cooled (−78° C.) solution of the cyclic sulfate (1,2-$C_6H_4(CH_2O)_2SO_2$) (16.0 g, 80.2 mmol) in THF (200 mL). The mixture was stirred for 30 min at −78° C. and then stirred for 30 min at room temperature. After cooling the mixture to −78° C., it was treated with a solution of PyPhPLi {prepared from PyPhPH (15.1 g, 80.2 mmol) in THF (100 mL) and $Bu^nLi$ (32.1 ml of a 2.5M solution in hexane, 207.5 mmol) at −78° C.}. The mixture was allowed to warm to room temperature and then stirred overnight. The solvent was removed under reduced pressure and the residue was re-dissolved in $Et_2O$ (500 mL). The solution was then quenched with water (200 mL). The biphasic mixture was then stirred at room temperature for 30 minutes before the organic (upper) phase was cannula transferred into a clean Schlenk flask. The solvent was then removed under vacuum to give a brown/orange sticky solid. The solid was dissolved in TBME (600 ml) and tetrafluoroboric acid diethyl ether complex (481 mmol, 66 ml) was then added. This gave the immediate formation of an orange precipitate. The mixture was then heated to reflux for 16 hours. The solvent was then removed under vacuum and the residue treated with a solution of potassium hydroxide (40 g, 713 mmol) in water (300 ml, degassed with nitrogen gas for 30 minutes). Pentane (500 ml) was then added and the biphasic mixture rapidly stirred for thirty minutes. The upper phase (organic) was then cannula transferred into a clean Schlenk flask and the solvent removed under vacuum. This gave a viscous orange oil, yield=7.9 g, 23% $^{31}P\{^{1}H\}$NMR (121 MHz, $CDCl_3$) ä: −10.0 (s, PPyPh); 28.2 (s, $PBu^t$)

CARBONYLATION EXAMPLES

General

Carbonylation is carried out as follows and the results with the ligands of examples and comparative examples are shown in tables.

Experimental

1.0 Reactions using 1-(di-t-butylphosphinomethyl)-2-(di-pyridin-2-ylphosphinomethyl)benzene (TPhos) and (di-t-butylphosphinomethyl)benzene (Alpha) with Trifluoroacetic acid (TFA)

Using standard Schlenk line techniques, reaction solutions were prepared by dissolving 7.7 mg $Pd_2(dba)_3$ ($1.46\times10^{-5}$

moles Pd) and either 28.9 mg (di-t-butylphosphinomethyl) benzene (Alpha) ($7.29\times10^{-5}$ moles) or 31.8 mg 1-(di-t-butylphosphinomethyl)-2-(di-pyridin-2-ylphosphinomethyl) benzene (TPhos) ($7.29\times10^{-5}$ moles) dissolved in a 70:30% w/w solvent composition of methyl propionate and methanol, in a total solution volume of 300 ml. The palladium and ligand were allowed to complex before the addition of trifluoroacetic acid (TFA) completed the preparation of the catalyst solution.

The catalytic solution was added to the pre-evacuated autoclave and the reactants were heated to 100° C. with stirring at 1000 rpm. Next the reaction vessel was pressurised with 8 bars of ethene above the solvent vapour pressure (2.3 bar at 100° C.), and the catalyst solution was stirred for 20 mins. After pre-treatment with ethene the reaction was initiated by pressurising the reactor to 12.3 bar with a 1:1 molar mixture of CO and ethene, to afford an initial 9:1 gas phase molar ratio of ethylene:CO. The total reaction pressure (12.3 bar) was maintained throughout the batch study with the use of a Tescom regulatory valve attached to a 1:1 molar CO/ethene 10 L reservoir. Both the reaction TON and rate can be obtained by measuring the drop in the reservoir pressure and assuming ideal gas behaviour and 100% selectivity for methyl propionate. After the reaction period, the autoclave was cooled and vented.

TABLE 1

| Summary of 1.0 conditions. | |
|---|---|
| Catalyst Conc^n^ ($mol \cdot dm^{-3}$) | $4.90 \times 10^{-5}$ |
| Total ligand($L_2$)/Pd | 5:1 |
| Total $H^+$/Pd | x:1 see table 5 |
| Pressure (bar) | 12.3 |
| Temperature (° C.) | 100 |
| Headspace $C_2H_4$/CO | 9:1 |

$L_2$ Ligand
$H^+$ Propionic Acid

## 2.0 Reactions using 1-(di-t-butylphosphinomethyl)-2-(di-pyridin-2-ylphosphinomethyl)benzene (TPhos) and Methanesulphonic acid (MSA)

Using standard Schlenk line techniques, reaction solutions were prepared by dissolving 7.7 mg $Pd_2(dba)_3$ ($1.46\times10^{-5}$ moles Pd) and 31.8 mg 1-(di-t-butylphosphinomethyl)-2-(di-pyridin-2-ylphosphinomethyl)benzene (TPhos) ($7.29\times10^{-5}$ moles) dissolved in a solvent composition of methyl propionate and methanol which was varied between 90:10% w/w and 50:50% w/w. The total solution volume was kept constant (300 ml). The palladium and ligand were allowed to complex before the addition of 430 μl ($6.56\times10^{-3}$ moles) methanesulphonic acid (MSA) completed the preparation of the catalyst solution. The catalytic solution was added to the pre-evacuated autoclave and the reactants were heated to 100° C. with stirring at 1000 rpm. Next the reaction vessel was pressurised with 8 bars of ethene above the solvent vapour pressure (2.3 bar at 100° C.), and the catalyst solution was stirred for 20 mins. After pre-treatment with ethene the reaction was initiated by pressurising the reactor to 12.3 bar with a 1:1 molar mixture of CO and ethene, to afford an initial 9:1 gas phase molar ratio of ethylene:CO. The total reaction pressure (12.3 bar) was maintained throughout the batch study with the use of a Tescom regulatory valve attached to a 1:1 molar CO/ethene 10 L reservoir. Both the reaction TON and rate can be obtained by measuring the drop in the reservoir pressure and assuming ideal gas behaviour and 100% selectivity for methyl propionate. After the reaction period, the autoclave was cooled and vented.

TABLE 2

| Summary of 2.0 conditions. | |
|---|---|
| Catalyst Conc^n^ ($mol \cdot dm^{-3}$) | $4.90 \times 10^{-5}$ |
| Total $L_2$/Pd | 5:1 |
| Total $H^+$/Pd | 450:1 |
| Pressure (bar) | 12.3 |
| Temperature (° C.) | 100 |
| Headspace $C_2H_4$/CO | 9:1 |

$L_2$ Ligand
$H^+$ Propionic Acid

## 3.0 Initial Reactions using 1-(di-t-butylphosphinomethyl)-2-(di-pyridin-2-ylphosphinomethyl)benzene (TPhos) and (di-t-butylphosphinomethyl)benzene (Alpha) with Propionic acid (PA)

Using standard Schlenk line techniques, reaction solutions were prepared by dissolving 77 mg $Pd_2(dba)_3$ ($1.46\times10^{-4}$ moles Pd) and either 289 mg (di-t-butylphosphinomethyl) benzene ($7.29\times10^{-4}$ moles) or 318 mg TPhos ($7.29\times10^{-4}$ moles) dissolved in a 70:30 w/w solvent composition of methyl propionate and methanol, in a total solution volume of 300 ml. The palladium and ligand were allowed to complex before the addition of 70 ml ($9.33\times10^{-1}$ moles) propionic acid (PA). The catalytic solution was added to the pre-evacuated autoclave and the reactants were heated to 100° C. with stirring at 1000 rpm. Next the reaction vessel was pressurised with 8 bars of ethene above the solvent vapour pressure (2.3 bar at 100° C.), and the catalyst solution was stirred for 20 mins. After pre-treatment with ethene the reaction was initiated by pressurising the reactor to 12.3 bar with a 1:1 molar mixture of CO and ethene, to afford an initial 9:1 gas phase molar ratio of ethylene:CO. The total reaction pressure (12.3 bar) was maintained throughout the batch study with the use of a Tescom regulatory valve attached to a 1:1 molar CO/ethene 10 L reservoir. Both the reaction TON and rate can be obtained by measuring the drop in the reservoir pressure and assuming ideal gas behaviour and 100%; selectivity for methyl propionate. After the reaction period, the autoclave was cooled and vented.

TABLE 3

| Summary of 3.0 conditions. | |
|---|---|
| Catalyst Conc^n^ ($mol \cdot dm^{-3}$) | $4.90 \times 10^{-4}$ |
| Total $L_2$/Pd | 5:1 |
| Total $H^+$/Pd | ~6400:1 |
| Pressure (bar) | 12.3 |
| Temperature (° C.) | 100 |
| Headspace $C_2H_4$/CO | 9:1 |

$L_2$ Ligand
$H^+$ Propionic Acid

## 4.0 Further Specific Reactions using 1-(di-t-butylphosphinomethyl)-2-(di-pyridin-2-ylphosphinomethyl)benzene (TPhos) and (di-t-butylphosphinomethyl)benzene (Alpha) with Propionic acid (PA)

Using standard Schlenk line techniques, reaction solutions were prepared by dissolving 77 mg $Pd_2(dba)_3$ ($1.46\times10^{-4}$ moles Pd) and either 289 mg (di-t-butylphosphinomethyl) benzene ($7.29\times10^{-4}$ moles) or 318 mg TPhos ($7.29\times10^{-4}$ moles) dissolved in a 70:30 w/w solvent composition of methyl propionate and methanol, in a total solution volume of 300 ml. The palladium and ligand were allowed to complex before the addition of propionic acid (PA). The catalytic solution was added to the pre-evacuated autoclave and the reactants were heated to 100° C. with stirring at 1000 rpm. Next the reaction vessel was pressurised with 8 bars of ethene above the solvent vapour pressure (2.3 bar at 100° C.), and the catalyst solution was stirred for 20 mins. After pre-treatment with ethene the reaction was initiated by pressurising the reactor to 12.3 bar with a 1:1 (gas molar ratio) mixture of CO and ethene, to afford an initial 9:1 gas molar ratio of ethylene: CO in the gas phase of the reactor. The total reaction pressure (12.3 bar) was maintained throughout the batch study with the use of a Tescom regulatory valve attached to a 1:1 gas molar ratio CO/ethene 10 L reservoir. Both the reaction TON and rate can be obtained by measuring the drop in the reservoir pressure and assuming ideal gas behaviour and 100% selectivity for methyl propionate. After the reaction period, the autoclave was cooled and vented.

TABLE 4

Summary of 4.0 conditions.

| | |
|---|---|
| Catalyst Conc$^n$ (mol · dm$^{-3}$) | 4.90 x $10^{-4}$ |
| Total $L_2$/Pd | 5:1 |
| Total $H^+$/Pd | x:1 see table 8 |
| Pressure (bar) | 12.3 |
| Temperature (° C.) | 100 |
| Headspace $C_2H_4$/CO (molar ratio) | 9:1 |

$L_2$ Ligand
$H^+$ Propionic Acid

## Results

### 1.0 Results of Reactions using 1-(di-t-butylphosphinomethyl)-2-(di-pyridin-2-ylphosphinomethyl)benzene (TPhos) and (di-t-butylphosphinomethyl)benzene (Alpha) with Trifluoroacetic acid (TFA)

The results are presented in Table 5 and Table 6. TPhos has been shown to outperform (di-t-butylphosphinomethyl)benzene comparative example by a 3 to 4 fold margin in the relatively weak acid TFA.

TABLE 5

| | Example 1 TPhos 1000 eq of TFA (1.083 cm$^3$) | Example 2 TPhos 2000 eq of TFA (2.166 cm$^3$) | Example 3 TPhos 4500 eq of TFA (4.870 cm$^3$) |
|---|---|---|---|
| Rate (mol MeP/mol Pd/hr) | 46602 | 47611 | 41386 |
| TON (moles MeP/mole Pd) | 15570 | 15378 | 21038 |

TABLE 6

| | Comparative Example 4 Alpha 1000 eq of TFA (1.083 cm$^3$) | Comparative Example 5 Alpha 4500 eq of TFA (4.870 cm$^3$) |
|---|---|---|
| Rate (mol MeP/mol Pd/hr) | 1911 | 10696 |
| TON moles MeP/mole Pd | 3407 | 11038 |

### 2.0 Results of Reactions using 1-(di-t-butylphosphinomethyl)-2-(di-pyridin-2-ylphosphinomethyl)benzene (TPhos) and Methanesulphonic acid (MSA)

The results are presented in Table 7

TABLE 7

| MeP/MeOH % w/w | Initial Rate (mol MeP/mol Pd/hr) | TON moles MeP/mole Pd |
|---|---|---|
| 50/50 | 68557 | 59137 |
| 70/30 | 39771 | 33456 |
| 80/20 | 23524 | 23397 |
| 90/10 | 11496 | 10151 |

The data in table 7 show that the ligand 1-(di-t-butylphosphinomethyl)-2-(di-pyridin-2-ylphosphinomethyl)benzene (TPhos) has good activity when used with methanesulphonic acid.

### 3.0 Initial Propionic Acid Reactions

The results of the initial study conducted using $1.46\times10^{-4}$ moles Pd and a Palladium concentration of $3.90\times10^{-4}$ mol·dm$^{-3}$ were that TPhos was found to display higher rates and dramatically improved TON compared with (di-t-butylphosphinomethyl)benzene in propionic acid (PA).

### 4.0 Results of further reactions using 1-(di-t-butylphosphinomethyl)-2-(di-pyridin-2-ylphosphinomethyl)benzene (TPhos) and (di-t-butylphosphinomethyl)benzene (Alpha) with Propionic acid (PA)

TABLE 8

| | Example 1 TPhos 3213 mole eq of PA (35 cm$^3$) to Pd | Example 2 TPhos 6427 mole eq of PA (70 cm$^3$) to Pd | Example 3 TPhos 12854 mole eq of PA (140 cm$^3$) to Pd |
|---|---|---|---|
| Rate (mol MeP/mol Pd/hr) | 474 | 3286 | 3300 |
| TON (moles MeP/mole Pd) | 880 | 2340 | 2376 |

TABLE 9

| | Comparative Example 4 Alpha 6427 mole eq of PA (70 cm$^3$) to Pd | Comparative Example 5 Alpha 12854 mole eq of PA (140 cm$^3$) to Pd |
|---|---|---|
| Rate (mol MeP/mol Pd/hr) | 557 | 1128 |
| TON moles MeP/mole Pd | 560 | 1230 |

The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

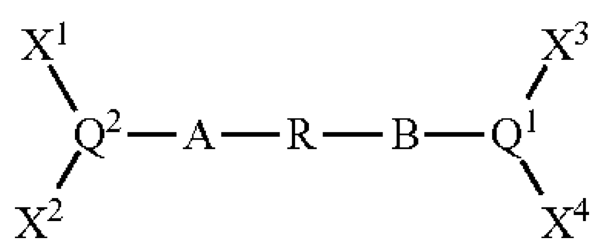
All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

The invention claimed is:

**1**. A bidentate ligand of formula (I)




(I)

wherein:

A and B each independently represent a direct bond or a lower alkylene linking group having from 1 to 10 carbons;

R represents a hydrocarbyl aromatic structure having at least one aromatic ring which is part of a metallocene complex and to which $Q^1$ and $Q^2$ are each linked, through B and A, respectively, on available adjacent atoms of the at least one aromatic ring;

the groups $X^3$ and $X^4$ independently represent univalent radicals of up to 30 atoms having at least one tertiary carbon atom or $X^3$ and $X^4$ together form a bivalent radical of up to 40 atoms having at least two tertiary carbon atoms wherein each said univalent or bivalent radical is joined via said at least one or two tertiary carbon atoms respectively to the respective atom $Q^1$;

the group $X^1$ is defined as a univalent hydrocarbyl radical of up to 30 atoms containing at least one nitrogen atom having a pKb in dilute aqueous solution at 18° C. of between 4 and 14 wherein the said at least one nitrogen atom is separated from the $Q^2$ atom by between 1 and 3 carbon atoms, wherein the group $X^1$ is selected from the group consisting of an aromatic nitrogen heterocycle having 3-14 ring atoms, aziridine, azirine, azetidine, azete, pyrrolidone, piperidine, azepane, azepine, azocane, azocine imidazolidine, pyrazolidine, imidazoline, pyrazoline, piperazine, hexahydro-pyrimidine, hexahydro-pyridazine, and pyrrolidine radicals;

the group $X^2$ is defined as $X^1$, $X^3$ or $X^4$ or represents a univalent radical of up to 30 atoms having at least one primary, secondary or aromatic ring carbon atom wherein each said univalent radical is joined via said at least one primary, secondary or aromatic ring carbon atom(s) respectively to the respective atom $Q^2$; and

$Q^1$ and $Q^2$ each independently represent phosphorus, arsenic or antimony.

**2**. The bidentate ligand according to claim **1**, wherein $X^2$ is the same group as $X^1$.

**3**. The bidentate ligand according to claim **1** selected from the group consisting of 1-(di-tert-butylphosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)ferrocene, 1-(di-tert-pentylphosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl) ferrocene, 1-(diadamantylphosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)ferrocene, 1-(di-3,5-dimethyladamantylphosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)ferrocene, 1-(di-5-tert-butyladamantylphosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)ferrocene, 1-(1-adamantyl tert-butyl-phosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl) ferrocene, 1-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one)-2-(di-pyridin-2-yl-phosphino)-1,2-dimethylferrocene, 1-(2-(phospha-adamantyl))-2-(di-pyridin-2-ylphosphino)-1,2-dimethylferrocene, 1-(dicongressylphosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)ferrocene, 1-(di-pyridin-2-yl-phosphinomethyl)-2,3-bis-(ditertbutylphosphinomethyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-1'-phenylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyridin-2-ylphosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyridin-2-ylphosphinomethyl)-1-(trimethylsilyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-1-(2'-phenylprop-2'-yl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-4,5-di-t-butylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-4-t butylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-1'-t-butylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyridin-2-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyridin-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyridin-2-yl-phosphinomethyl)-1-phenylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyridin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyridin-2-yl-phosphinomethyl) 4-(trimethylsilyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyridin-2-yl-phosphinomethyl)-1'-(trimethylsilyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyridin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyridin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyridin-2-yl-phosphinomethyl)-1'-(2'-phenylprop-2'-yl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyridin-2-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyridin-2-yl-phosphinomethyl)-4-t butylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyridin-2-yl-phosphinomethyl)-1'-t-butylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-4,5 diphenylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-1'-phenylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-4,5 bis-(trimethylsilyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-1'-(trimethylsilyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-1'-(2'-phenylprop-2'-yl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-4-t butylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-1'-t-butylferrocene, 1-(P,P adamantyl, t-butyl phosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(P,P adamantyl, t-butyl phosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-4-phenylferrocene, t-butyl phosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-1-phenylferrocene, 1-(P,P-adamantyl, t-butyl phosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(P,P adamantyl, t-butyl phosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(P,P adamantyl, t-butyl phosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-1'-(trimethylsilyl)ferrocene, 1-(P,P adamantyl, t-butyl phosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(P,P adamantyl, t-butyl phosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(P,P-adamantyl, t-butyl phosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-1'-(2'-phenylprop-2'-yl)ferrocene, 1-(P,P-adamantyl, t-butyl phosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, 1-(P,P-adamantyl, t-butyl phosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-4-t butylferrocene, 1-(P,P-adamantyl, t-butyl phosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)-1'-t-butylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyridin-2-yl-phosphinomethyl)-4,5-diphenyl-methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyridin-2-ylphosphinomethyl)-4-phenyl-methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyridin-2-ylphosphinomethyl)-1'-phenyl-methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyridin-2-yl-phosphinomethyl)-4,5-bis(trimethylsilyl)-methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyridin-2-ylphosphinomethyl)-4-(trimethylsilyl)-methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyridin-2-ylphosphinomethyl)-1'-(trimethylsilyl)-methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyridin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)-methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyridin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)-methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyridin-2-yl-phosphinomethyl)-1'-(2'-phenylprop-2'-yl)-methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyridin-2-yl-phosphinomethyl)-4,5-(di-t-butyl)-methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyridin-2-yl-phosphinomethyl)-4-t-butyl-methylferrocene, and 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyridin-2-yl-phosphinomethyl)-1'-t-butyl-methylferrocene.

**4**. The bidentate ligand according to claim **1** wherein A and B are methylene.

**5**. The bidentate ligand according to claim **1**, wherein $Q^1$ and $Q^2$ are each phosphorous.

**6**. The bidentate ligand according to claim **1** being 1-(di-tert-butylphosphinomethyl)-2-(pyridin-2-yl-phenylphosphinomethyl)ferrocene.

**7**. The bidentate ligand according to claim **1** being 1-(di-t-butylphosphinomethyl)-2-(di-pyridin-2-yl-phosphinomethyl)ferrocene.

**8**. The bidentate ligand according to claim **1** selected from the group consisting of 1-(di-tert-butylphosphinomethyl)-2-(di-pyridin-3-yl-phosphinomethyl)ferrocene, 1-(di-tert-pentylphosphinomethyl)-2-(di-pyridin-3-yl-phosphinomethyl) ferrocene, 1-(diadamantylphosphinomethyl)-2-(di-pyridin-3-yl-phosphinomethyl)ferrocene, 1-(di-3,5-dimethyladamantylphosphinomethyl)-2-(di-pyridin-3-yl-phosphinomethyl)ferrocene, 1-(di-5-tert-butyladamantylphosphinomethyl)-2-(di-pyridin-3-yl-phosphinomethyl)ferrocene, 1-(1-adamantyl-tert-butyl-phosphinomethyl)-2-(di-pyridin-3-yl-phosphinomethyl) ferrocene, 1-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one)-2-(di-pyridin-3-yl-phosphino)-1,2-dimethylferrocene, 1-(2-(phospha-adamantyl))-2-(di-pyridin-3-yl-phosphino)-1,2-dimethylferrocene, 1-(dicongressylphosphinomethyl)-2-(di-pyridin-3-yl-phosphinomethyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyridin-3-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyridin-3-yl-phosphinomethyl)-4-phenylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyridin-3-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyridin-3-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyridin-3-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyridin-3-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl) ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyridin-3-yl-phosphinomethyl)-4,5-di-t-butylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyridin-3-yl-phosphinomethyl)-4-t-butylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyridin-3-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyridin-3-yl-phosphinomethyl)-4-phenylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyridin-3-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyridin-3-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyridin-3-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyridin-3-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyridin-3-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyridin-3-yl-phosphinomethyl)-4-t-butylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyridin-3-yl-phosphinomethyl)-4,5 diphenylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyridin-3-yl-phosphinomethyl)-4-phenylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyridin-3-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyridin-3-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyridin-3-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyridin-3-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyridin-3-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyridin-3-yl-phosphinomethyl)-4-t-butylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyridin-3-yl-phosphinomethyl)-4,5-diphenylmethylferrocene, 1 (P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyridin-3-yl-phosphinomethyl)-4-phenyl-methylferrocene, 1 (P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyridin-3-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl) methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyridin-3-yl-phosphinomethyl)-4-(trimethylsilyl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyridin-3-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl) methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyridin-3-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyridin-3-yl-phosphinomethyl)-4,5-(di-t-butyl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyridin-3-yl-phosphinomethyl)-4-t-butylmethylferrocene, 1-(P,P-adamantyl-t-butyl phosphinomethyl)-2-(di-pyridin-3-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyridin-3-yl-phosphinomethyl)-4-phenylferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyridin-3-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(P,P-adamantly-t-butyl-phosphinomethyl)-2-(di-pyridin-3-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(P,P-adamantyl-t-butyl phosphinomethyl)-2-(di-pyridin-3-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyridin-3-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(P,P-adamantly-t-butyl-phosphinomethyl)-2-(di-pyridin-3-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, and 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyridin-3-yl-phosphinomethyl)-4-t-butylferrocene.

**9**. The bidentate ligand according to claim **1** selected from the group consisting of 1-(di-tert-butylphosphinomethyl)-2-(di-piperidin-2-yl-phosphinomethyl)ferrocene, 1-(di-tert-pentylphosphinomethyl)-2-(di-piperidin-2-yl-phosphinomethyl)ferrocene, 1-(diadamantylphosphinomethyl)-2-(di-piperidin-2-yl-phosphinomethyl)ferrocene, 1-(di-3,5-dimethyladamantylphosphinomethyl)-2-(di-piperidin-2-yl-phosphinomethyl)ferrocene, 1-(di-5-tert-butyladamantylphosphinomethyl)-2-(di-piperidin-2-yl-phosphinomethyl)ferrocene, 1-(1 adamantyl-tert-butyl-phosphinomethyl)-2-(di-piperidin-2-yl-phosphinomethyl) ferrocene, 1-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one)-2-(di-piperidin-2-yl-phosphino)-1,2-dimethylferrocene, 1-(2-(phospha-adamantyl))-2-(di-piperidin-2-yl-phosphino)-1,2-dimethylferrocene, 1-(dicongressylphosphinomethyl)-2-(di-piperidin-2-yl-phosphinomethyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-piperidin-2-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-piperidin-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-piperidin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-piperidin-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-piperidin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-piperidin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-piperidin-2-yl-phosphinomethyl)-4,5-di-t-butylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-piperidin-2-yl-phosphinomethyl)-4-t-butylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-piperidin-2-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-piperidin-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-piperidin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-piperidin-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-piperidin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-piperidin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-piperidin-2-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-piperidin-2-yl-phosphinomethyl)-4-t-butylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-piperidin-2-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-piperidin-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-piperidin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-piperidin-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-piperidin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-piperidin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-piperidin-2-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-piperidin-2-yl-phosphinomethyl)-4-t-butylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-piperidin-2-yl-phosphinomethyl)-4,5-diphenylmethylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-piperidin-2-yl-phosphinomethyl)-4-phenylmethylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-piperidin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-piperidin-2-yl-phosphinomethyl)-4-(trimethylsilyl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-piperidin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl) methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-piperidin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-piperidin-2-yl-phosphinomethyl)-4,5-(di-t-butyl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-piperidin-2-yl-phosphinomethyl)-4-t-butylmethylferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-piperidin-2-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(P,P-adamantyl, t-butyl-phosphinomethyl)-2-(di-piperidin-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-piperidin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(P,P-adamantyl-t-butyl phosphinomethyl)-2-(di-piperidin-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-piperidin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-piperidin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-piperidin-2-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, and 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-piperidin-2-yl-phosphinomethyl)-4-t-butylferrocene.

**10**. The bidentate ligand according to claim **1** selected from the group consisting of 1-(di-tert-butylphosphinomethyl)-2-(di-piperidin-3-yl-phosphinomethyl)ferrocene, 1-(di-tert-pentylphosphinomethyl)-2-(di-piperidin-3-yl-phosphinomethyl)ferrocene, 1-(diadamantylphosphinomethyl)-2-(di-piperidin-3-yl-phosphinomethyl)ferrocene, 1-(di-3,5-dimethyladamantylphosphinomethyl)-2-(di-piperidin-3-yl-phosphinomethyl)ferrocene, 1-(di-5-tert-butyladamantylphosphinomethyl)-2-(di-piperidin-3-yl-phosphinomethyl)ferrocene, 1-(1 adamantyl-tert-butyl-phosphinomethyl)-2-(di-piperidin-3-yl-phosphinomethyl) ferrocene, 1-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one)-2-(di-piperidin-3-yl-phosphino)-1,2-dimethylferrocene, 1-(2-(phospha-adamantyl))-2-(di-piperidin-3-yl-phosphino)-1,2-dimethylferrocene, 1-(dicongressylphosphinomethyl)-2-(di-piperidin-3-yl-phosphinomethyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-piperidin-3-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-piperidin-3-yl-phosphinomethyl)-4-phenylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-piperidin-3-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-piperidin-3-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-piperidin-3-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-piperidin-3-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-piperidin-3-yl-phosphinomethyl)-4,5-di-t-butylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-piperidin-3-yl-phosphinomethyl)-4-t-butylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-piperidin-3-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-piperidin-3-yl-phosphinomethyl)-4-phenylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-piperidin-3-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-piperidin-3-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-piperidin-3-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-piperidin-3-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-piperidin-3-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-piperidin-3-yl-phosphinomethyl)-4-t-butylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-piperidin-3-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-piperidin-3-yl-phosphinomethyl)-4-phenylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-piperidin-3-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-piperidin-3-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-piperidin-3-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-piperidin-3-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-piperidin-3-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-piperidin-3-yl-phosphinomethyl)-4-t-butylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-piperidin-3-yl-phosphinomethyl)-4,5-diphenylmethylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-piperidin-3-yl-phosphinomethyl)-4-phenylmethylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-piperidin-3-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-piperidin-3-yl-phosphinomethyl)-4-(trimethylsilyl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-piperidin-3-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl) methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-piperidin-3-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-piperidin-3-yl-phosphinomethyl)-4,5-(di-t-butyl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-piperidin-3-yl-phosphinomethyl)-4-t-butylmethylferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-piperidin-3-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-piperidin-3-yl-phosphinomethyl)-4-phenylferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-piperidin-3-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(P,P-adamantyl-t-butyl phosphinomethyl)-2-(di-piperidin-3-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-piperidin-3-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-piperidin-3-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-piperidin-3-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, and adamantyl, t 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-piperidin-3-yl-phosphinomethyl)-4-t-butylferrocene.

**11**. The bidentate ligand according to claim **1** selected from the group consisting of 1-(di-tert-butylphosphinomethyl)-2-(di-pyrrol-2-yl-phosphinomethyl)ferrocene, 1-(di-tert-pentylphosphinomethyl)-2-(di-pyrrol-2-yl-phosphinomethyl) ferrocene, 1-(diadamantylphosphinomethyl)-2-(di-pyrrol-2-yl-phosphinomethyl)ferrocene, 1-(di-3,5-dimethyladamantylphosphinomethyl)-2-(di-pyrrol-2-yl-phosphinomethyl)ferrocene, 1-(di-5-tert-butyladamantylphosphinomethyl)-2-(di-pyrrol-2-yl-phosphinomethyl)ferrocene, 1-(1-adamantyl tert-butyl-phosphinomethyl)-2-(di-pyrrol-2-yl-phosphinomethyl) ferrocene, 1-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one)-2-(di-pyrrol-2-yl-phosphino)-1,2-dimethylferrocene, 1-(2-(phospha-adamantyl))-2-(di-pyrrol-2-yl-phosphino)-1,2-dimethylferrocene, 1-(dicongressylphosphinomethyl)-2-(di-pyrrol-2-yl-phosphinomethyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrrol-2-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrrol-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrrol-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrrol-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrrol-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrrol-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrrol-2-yl-phosphinomethyl)-4,5-di-t-butylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrrol-2-yl-phosphinomethyl)-4-t-butylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrrol-2-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrrol-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrrol-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrrol-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrrol-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrrol-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrrol-2-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrrol-2-yl-phosphinomethyl)-4-t-butylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrrol-2-yl-phosphinomethyl)-4,5 diphenylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrrol-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrrol-2-yl-phosphinomethyl)-4,5 bis-(trimethylsilyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrrol-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrrol-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrrol-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrrol-2-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrrol-2-yl-phosphinomethyl)-4-t-butylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrrol-2-yl-phosphinomethyl)-4,5-diphenylmethylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrrol-2-yl-phosphinomethyl)-4-phenylmethylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrrol-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrrol-2-yl-phosphinomethyl)-4-(trimethylsilyl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrrol-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrrol-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrrol-2-yl-phosphinomethyl)-4,5-(di-t-butyl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrrol-2-yl-phosphinomethyl)-4-t-butylmethylferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrrol-2-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrrol-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrrol-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrrol-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrrol-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrrol-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrrol-2-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, and 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrrol-2-yl-phosphinomethyl)-4-t-butylferrocene.

**12**. The bidentate ligand according to claim **1** selected from the group consisting of 1-(di-tert-butylphosphinomethyl)-2-(di-pyrrol-3-yl-phosphinomethyl)ferrocene, 1-(di-tert-pentylphosphinomethyl)-2-(di-pyrrol-3-yl-phosphinomethyl) ferrocene, 1-(diadamantylphosphinomethyl)-2-(di-pyrrol-3-yl-phosphinomethyl)ferrocene, 1-(di-3,5-dimethyladamantylphosphinomethyl)-2-(di-pyrrol-3-yl-phosphinomethyl)ferrocene, 1-(di-5-tert-butyladamantylphosphinomethyl)-2-(di-pyrrol-3-yl-phosphinomethyl)ferrocene, 1-(1-adamantyl tert-butyl-phosphinomethyl)-2-(di-pyrrol-3-yl-phosphinomethyl) ferrocene, 1-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one)-2-(di-pyrrol-3-yl-phosphino)-1,2-dimethylferrocene, 1-(2-(phospha-adamantyl))-2-(di-pyrrol-3-yl-phosphino)-1,2-dimethylferrocene, 1-(dicongressylphosphinomethyl)-2-(di-pyrrol-3-yl-phosphinomethyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrrol-3-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrrol-3-yl-phosphinomethyl)-4-phenylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrrol-3-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrrol-3-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrrol-3-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrrol-3-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrrol-3-yl-phosphinomethyl)-4,5-di-t-butylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrrol-3-yl-phosphinomethyl)-4-t-butylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrrol-3-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrrol-3-yl-phosphinomethyl)-4-phenylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrrol-3-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrrol-3-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrrol-3-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrrol-3-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrrol-3-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrrol-3-yl-phosphinomethyl)-4-t-butylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrrol-3-yl-phosphinomethyl)-4,5 diphenylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrrol-3-yl-phosphinomethyl)-4-phenylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrrol-3-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrrol-3-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrrol-3-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrrol-3-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrrol-3-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrrol-3-yl-phosphinomethyl)-4-t-butylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrrol-3-yl-phosphinomethyl)-4,5-diphenylmethylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrrol-3-yl-phosphinomethyl)-4-phenylmethylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrrol-3-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl) methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrrol-3-yl-phosphinomethyl)-4-(trimethylsilyl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrrol-3-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl) methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrrol-3-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrrol-3-yl-phosphinomethyl)-4,5-(di-t-butyl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrrol-3-yl-phosphinomethyl)-4-t-butylmethylferrocene, 1-(P,P adamantyl, t-butyl phosphinomethyl)-2-(di-pyrrol-3-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrrol-3-yl-phosphinomethyl)-4-phenylferrocene, 1-(P,P-adamantyl-t-butyl phosphinomethyl)-2-(di-pyrrol-3-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrrol-3-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrrol-3-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrrol-3-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrrol-3-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, and 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrrol-3-yl-phosphinomethyl)-4-t-butylferrocene.

**13**. The bidentate ligand according to claim **1** selected from the group consisting of 1-(di-tert-butylphosphinomethyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)ferrocene, 1-(di-tert-pentylphosphinomethyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)ferrocene, 1-(diadamantylphosphinomethyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)ferrocene, 1-(di-3,5-dimethyladamantylphosphinomethyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)ferrocene, 1-(di-5-tert-butyladamantylphosphinomethyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)ferrocene, 1-(1 adamantyl-tert-butyl-phosphinomethyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl) ferrocene, 1-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one)-2-(di-pyrrolidin-2-yl-phosphino)-1,2-dimethylferrocene, 1-(2-(phospha-adamantyl))-2-(di-pyrrolidin-2-yl-phosphino)-1,2-dimethylferrocene, 1-(dicongressylphosphinomethyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4,5-di-t-butylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4-t-butylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4-t-butylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4-t-butylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4,5-diphenylmethylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4-phenylmethylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4-(trimethylsilyl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl) methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4,5-(di-t-butyl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4-t-butylmethylferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(P,P-adamantyl-t-butyl phosphinomethyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, and adamantyl, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrrolidin-2-yl-phosphinomethyl)-4-t-butylferrocene.

**14**. The bidentate ligand according to claim **1** selected from the group consisting of 1-(di-tert-butylphosphinomethyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)ferrocene, 1-(di-tert-pentylphosphinomethyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)ferrocene, 1-(diadamantylphosphinomethyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)ferrocene, 1-(di-3,5-

dimethyladamantylphosphinomethyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)ferrocene, 1-(di-5-tert-butyladamantylphosphinomethyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)ferrocene, 1-(1 adamantyl-tert-butyl-phosphinomethyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl) ferrocene, 1-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one)-2-(di-pyrrolidin-3-yl-phosphino)-1,2-dimethylferrocene, 1-(2-(phospha-adamantyl))-2-(di-pyrrolidin-3-yl-phosphino)-1,2-dimethylferrocene, 1-(dicongressylphosphinomethyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4-phenylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4,5-di-t-butylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4-t-butylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4-phenylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4-t-butylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4,5 diphenylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4-phenylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4-t-butylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4,5-diphenylmethylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4-phenylmethylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4-(trimethylsilyl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl) methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4,5-(di-t-butyl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4-t-butylmethylferrocene, 1-(P,P-adamantyl-t-butyl phosphinomethyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4-phenylferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(P,P-adamantyl-t-butyl phosphinomethyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, and adamantyl, 1-(P,P-adamantyl-t-butyl phosphinomethyl)-2-(di-pyrrolidin-3-yl-phosphinomethyl)-4-t-butylferrocene.

**15**. The bidentate ligand according to claim **1** selected from the group consisting of 1-(di-tert-butylphosphinomethyl)-2-(di-quinolin-2-yl-phosphinomethyl)ferrocene, 1-(di-tert-pentylphosphinomethyl)-2-(di-quinolin-2-yl-phosphinomethyl)ferrocene, 1-(diadamantylphosphinomethyl)-2-(di-quinolin-2-yl-phosphinomethyl)ferrocene, 1-(di-3,5-dimethyladamantylphosphinomethyl)-2-(di-quinolin-2-yl-phosphinomethyl)ferrocene, 1-(di-5-tert-butyladamantylphosphinomethyl)-2-(di-quinolin-2-yl-phosphinomethyl)ferrocene, 1-(1 adamantyl-tert-butyl-phosphinomethyl)-2-(di-quinolin-2-yl-phosphinomethyl) ferrocene, 1-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one)-2-(di-quinolin-2-yl-phosphino)-1,2-dimethylferrocene, 1-(2-(phospha-adamantyl))-2-(di-quinolin-2-yl-phosphino)-1,2-dimethylferrocene, 1-(dicongressylphosphinomethyl)-2-(di-quinolin-2-yl-phosphinomethyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-quinolin-2-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-quinolin-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-quinolin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-quinolin-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-quinolin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-quinolin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-quinolin-2-yl-phosphinomethyl)-4,5-di-t-butylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-quinolin-2-yl-phosphinomethyl)-4-t-butylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-quinolin-2-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-quinolin-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-quinolin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-quinolin-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(2-

phosphinomethyl-adamantyl)-2-(di-quinolin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-quinolin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-quinolin-2-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-quinolin-2-yl-phosphinomethyl)-4-t-butylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-quinolin-2-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-quinolin-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-quinolin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-quinolin-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-quinolin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-quinolin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-quinolin-2-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-quinolin-2-yl-phosphinomethyl)-4-t-butylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-quinolin-2-yl-phosphinomethyl)-4,5-diphenylmethylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-quinolin-2-yl-phosphinomethyl)-4-phenylmethylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-quinolin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl) methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-quinolin-2-yl-phosphinomethyl)-4-(trimethylsilyl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-quinolin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl) methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-quinolin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-quinolin-2-yl-phosphinomethyl)-4,5-(di-t-butyl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-quinolin-2-yl-phosphinomethyl)-4-t-butylmethylferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-quinolin-2-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-quinolin-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-Quinolin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-quinolin-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-quinolin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(P,P-adamantyl-t-butyl phosphinomethyl)-2-(di-quinolin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-quinolin-2-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, and 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-Quinolin-2-yl-phosphinomethyl)-4-t-butylferrocene.

**16**. The bidentate ligand according to claim **1** selected from the group consisting of 1-(di-tert-butylphosphinomethyl)-2-(di-pyrazin-2-yl-phosphinomethyl)ferrocene, 1-(di-tert-pentylphosphinomethyl)-2-(di-pyrazin-2-yl-phosphinomethyl) ferrocene, 1-(diadamantylphosphinomethyl)-2-(di-pyrazin-2-yl-phosphinomethyl)ferrocene, 1-(di-3,5-dimethyladamantylphosphinomethyl)-2-(di-pyrazin-2-yl-phosphinomethyl)ferrocene, 1-(di-5-tert-butyladamantylphosphinomethyl)-2-(di-pyrazin-2-yl-phosphinomethyl)ferrocene, 1-(1 adamantyl-tert-butyl-phosphinomethyl)-2-(di-pyrazin-2-yl-phosphinomethyl)ferrocene, 1-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one)-2-(di-pyrazin-2-yl-phosphino)-1,2-dimethylferrocene, 1-(2-(phospha-adamantyl))-2-(di-pyrazin-2-yl-phosphino)-1,2-dimethylferrocene, 1-(dicongressylphosphinomethyl)-2-(di-pyrazin-2-yl-phosphinomethyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrazin-2-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrazin-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrazin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrazin-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrazin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrazin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrazin-2-yl-phosphinomethyl)-4,5-di-t-butylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrazin-2-yl-phosphinomethyl)-4-t-butylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrazin-2-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrazin-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrazin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrazin-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrazin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrazin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrazin-2-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrazin-2-yl-phosphinomethyl)-4-t-butylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrazin-2-yl-phosphinomethyl)-4,5 diphenylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrazin-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrazin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrazin-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrazin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrazin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrazin-2-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrazin-2-yl-phosphinomethyl)-4-t-butylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrazin-2-yl-phosphinomethyl)-4,5-diphenylmethylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrazin-2-yl-phosphinomethyl)-4-phenylmethylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrazin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl) methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrazin-2-yl-phosphinomethyl)-4-(trimethylsilyl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrazin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl) methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrazin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrazin-2-

yl-phosphinomethyl)-4,5-(di-t-butyl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrazin-2-yl-phosphinomethyl)-4-t-butylmethylferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrazin-2-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(P,P-adamantyl-t-butyl phosphinomethyl)-2-(di-pyrazin-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(P, P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrazin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrazin-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrazin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(P,P-adamantyl-t-butyl phosphinomethyl)-2-(di-pyrazin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrazin-2-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, and 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrazin-2-yl-phosphinomethyl)-4-t-butylferrocene.

**17**. The bidentate ligand according to claim **1** selected from the group consisting of 1-(di-tert-butylphosphinomethyl)-2-(di-piperazin-2-yl-phosphinomethyl)ferrocene, 1-(di-tert-pentylphosphinomethyl)-2-(di-piperazin-2-yl-phosphinomethyl)ferrocene, 1-(diadamantylphosphinomethyl)-2-(di-piperazin-2-yl-phosphinomethyl)ferrocene, 1-(di-3,5-dimethyladamantylphosphinomethyl)-2-(di-piperazin-2-yl-phosphinomethyl)ferrocene, 1-(di-5-tert-butyladamantylphosphinomethyl)-2-(di-piperazin-2-yl-phosphinomethyl)ferrocene, 1-(1 adamantyl-tert-butyl-phosphinomethyl)-2-(di-piperazin-2-yl-phosphinomethyl) ferrocene, 1-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one)-2-(di-piperazin-2-yl-phosphino)-1,2-dimethylferrocene, 1-(2-(phospha-adamantyl))-2-(di-piperazin-2-yl-phosphino)-1,2-dimethylferrocene, 1-(dicongressylphosphinomethyl)-2-(di-piperazin-2-yl-phosphinomethyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-piperazin-2-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-piperazin-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-piperazin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-piperazin-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-piperazin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-piperazin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-piperazin-2-yl-phosphinomethyl)-4,5-di-t-butylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-piperazin-2-yl-phosphinomethyl)-4-t-butylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-piperazin-2-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-piperazin-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-piperazin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-piperazin-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-piperazin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-piperazin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-piperazin-2-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-piperazin-2-yl-phosphinomethyl)-4-t-butylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-piperazin-2-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-piperazin-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-piperazin-2-yl-phosphinomethyl)-4,5 bis-(trimethylsilyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-piperazin-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-piperazin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-piperazin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl) ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-piperazin-2-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-piperazin-2-yl-phosphinomethyl)-4-t-butylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-piperazin-2-yl-phosphinomethyl)-4,5-diphenylmethylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-piperazin-2-yl-phosphinomethyl)-4-phenylmethylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-piperazin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-piperazin-2-yl-phosphinomethyl)-4-(trimethylsilyl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-piperazin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl) methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-piperazin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-piperazin-2-yl-phosphinomethyl)-4,5-(di-t-butyl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-piperazin-2-yl-phosphinomethyl)-4-t-butylmethylferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-piperazin-2-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(P,P-adamantyl-t-butyl phosphinomethyl)-2-(di-piperazin-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-piperazin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-piperazin-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-piperazin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-piperazin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-piperazin-2-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, and adamantyl, 1-(P,P-adamantyl-t-butyl phosphinomethyl)-2-(di-piperazin-2-yl-phosphinomethyl)-4-t-butylferrocene.

**18**. The bidentate ligand according to claim **1** selected from the group consisting of 1-(di-tert-butylphosphinomethyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)ferrocene, 1-(di-tert-pentylphosphinomethyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)ferrocene, 1-(diadamantylphosphinomethyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)ferrocene, 1-(di-3,5-dimethyladamantylphosphinomethyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)ferrocene, 1-(di-5-tert-butyladamantylphosphinomethyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)ferrocene, 1-(1 adamantyl-tert-butyl-phosphinomethyl)-2-(di-pyrimidin-2-yl-phosphinomethyl) ferrocene, 1-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one)-2-(di-pyrimidin-2-yl-phosphino)-1,2-dimethylferrocene, 1-(2-(phospha-adamantyl))-2-(di-pyrimidin-2-yl-phosphino)-1,2-dimethylferrocene, 1-(dicongressylphosphinomethyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)-4,5-di-t-butylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)-4-t-butylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)-4-t-butylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)-4-t-butylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrimidin-2-yl-phosphinomethyl)-4,5-diphenylmethylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrimidin-2-yl-phosphinomethyl)-4-phenylmethylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrimidin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrimidin-2-yl-phosphinomethyl)-4-(trimethylsilyl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrimidin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrimidin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl) methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrimidin-2-yl-phosphinomethyl)-4,5-(di-t-butyl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-pyrimidin-2-yl-phosphinomethyl)-4-t-butylmethylferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(P,P-adamantyl, t-butyl-phosphinomethyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, and 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-pyrimidin-2-yl-phosphinomethyl)-4-t-butylferrocene.

**19**. The bidentate ligand according to claim **1** selected from the group consisting of 1-(di-tert-butylphosphinomethyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)ferrocene, 1-(di-tert-pentylphosphinomethyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)ferrocene, 1-(diadamantylphosphinomethyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)ferrocene, 1-(di-3,5-dimethyladamantylphosphinomethyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)ferrocene, 1-(di-5-tert-butyladamantylphosphinomethyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)ferrocene, 1-(1 adamantyl-tert-butyl-phosphinomethyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)ferrocene, 1-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one)-2-(di-hexahydro-pyrimidin-2-yl-phosphino)-1,2-dimethylferrocene, 1-(2-(phospha-adamantyl))-2-(di-hexahydro-pyrimidin-2-yl-phosphino)-1,2-dimethylferrocene, 1-(dicongressylphosphinomethyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4,5-di-t-butylferrocene, 1-(di-t-butylphosphinomethyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4-t-butylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl) ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, 1-(2-phosphinomethyl-adamantyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4-t-butylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4,5 diphenylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, 1-(di-adamantylphosphinomethyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4-t-butylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4,5-diphenylmethylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4-phenylmethylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4-(trimethylsilyl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4,5-(di-t-butyl)methylferrocene, 1-(P-(2,2,6,6-tetramethyl-phospha-cyclohexan-4-one))-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4-t-butylmethylferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4,5-diphenylferrocene, 1-(P,P-adamantly-t-butyl-phosphinomethyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4-phenylferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4,5-bis-(trimethylsilyl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4-(trimethylsilyl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4,5-di-(2'-phenylprop-2'-yl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4-(2'-phenylprop-2'-yl)ferrocene, 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4,5-(di-t-butyl)ferrocene, and 1-(P,P-adamantyl-t-butyl-phosphinomethyl)-2-(di-hexahydro-pyrimidin-2-yl-phosphinomethyl)-4-t-butylferrocene.

**20**. A process for the carbonylation of ethylenically unsaturated compounds comprising reacting said compound with carbon monoxide in the presence of a source of hydroxyl groups, optionally, a source of anions and of a catalyst system, the catalyst system obtainable by combining:

(a) a metal of Group 8, 9 or 10 of the Periodic Table or a compound thereof; and

(b) the bidentate ligand of formula (I) according to claim **1**.

**21**. A process for the carbonylation of ethylenically unsaturated compounds as claimed in claim **20**, wherein the catalyst system has a pKa in aqueous solution at 18° C. of between −2 and 6.

**22**. A process for the carbonylation of ethylenically unsaturated compounds as claimed in claim **20**, wherein the catalyst system has a pKa in aqueous solution at 18° C. of between 0 and 5.

**23**. The process for using the bidentate ligand according to claim **20** wherein A and B are methylene.

**24**. A novel complex comprising the bidentate ligand of formula I according to claim **1** coordinated to a metal of Group 8, 9 or 10 of the Periodic Table or a compound thereof.

**25**. A catalyst system for catalysing the carbonylation of an ethylenically unsaturated compound, the system is obtainable by combining:

a) a metal of Group 8, 9 or 10 of the Periodic Table or a compound thereof,

b) the bidentate ligand of formula I according to claim **1**, and

c) optionally, an acid.

**26**. The catalyst system according to claim **25**, wherein said acid has a pKa measured in dilute aqueous solution at 18° C. of between −2 and 6.

**27**. The catalyst system according to claim **25**, wherein said acid has a pKa measured in dilute aqueous solution at 18° C. of between 0 and 5.

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